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USSR REPORT CHEMISTRY

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MODIFIED STEROIDS, REPORT 18: STUDY OF OXIDATION REACTION OF STEROID
ALKALOID SOLASODIN AND ITS DERIVATIVES BY HYDROGEN PEROXIDE

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA
in Russian No 4, Jul-Aug 83 (manuscript received 25 Mar 82) pp 71-74

IRISMETOV, M. P., MIRZASALIYEVA, N. A., RUSTEMBEKOVA, G. B. and
BAZALITSKAYA, V. S., Institute of Chemical Sciences, KaSSR Academy of Sciences,
Alma-Ata

[Abstract] A study of the oxidation of solasodin and its derivatives by
hydrogen peroxide in glacial acetic acid is described. Oxidation by 30 percent
hydrogen peroxide in glacial acetic acid produced yields of triol, diol and
tetraol, after recrystallization from methanol, of less than 35-40 percent.
 R_f values of solasodin and products of its conversion were determined by thin-
layer chromatography, tabulated and discussed. Structure of the synthesized
compounds, determined by infra-red spectrography, were described. References
6 (Russian).
[381-2791]

APPLICATION OF THERMAL ANALYSIS METHODS IN STUDYING OIL SHALE

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 3 Nov 81, pp 28-35)

GONTSOV, A. A., SLAVGORODSKIY, N. I. and AMARSKIY, Ye. G., All-Union Scientific Research and Geological Study Institute for Coal Deposits; Rostov University

[Abstract] Thermal analysis has been used in combination with gas chromatography and other physical chemical methods to determine properties of oil shale and find optimum methods for processing it. The present study was devoted to comparative analysis of thermal destruction of oil shale from various deposits that differed according to geologic age, formation process and kerogen type and stage. Several similar oil shales from Volga basin deposits were tested. Analysis of derivatograms and other analyses indicated three stages of decomposition for carbonate shales and two for clay oil shales. Differential thermal analysis and thermal gravimetry determined moisture content of the shales. The shales were found to have varying thermal stability, with samples from Estonian deposits yielding some 95% of their total volatile products at 530-550°C and others being more stable. Pyrolysis and subsequent analysis of the gases produced showed that clay shales had increased hydrogen sulfide levels, while all tested shales contained heavy hydrocarbons in stable concentrations compared to methane. Carbonate shales released chiefly CO when decomposing at 750-1000°C. Release of volatile gases in decomposition in a vacuum corresponded to mass changes in shales at atmospheric pressure. Semicoking of oil shales from the Volga basin was judged to be promising. Figure 1; references 9 (Russian).
[376-12131]

STUDY OF STRUCTURE OF HIGH-BOILING-POINT PHENOLS SEPARATED FROM G6-GROUP COAL TAR

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 4 Dec 81) pp 144-150

PLATONOV, V. V., KLYAVINA, O. A., PROKOF'YEV, Ye. Ye. and IVLEVA, L. N.,
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[Abstract] The present study deals with phenols from the G6 group of the Kuznetsk basin with boiling points, above 523 K, and an average molecular weight of 248 units. Preliminary characteristics were determined by infrared spectroscopy, which indicated that these tars contained--along with phenol groups--quinoid, alcohol, and alkoxy groups, along with small amounts of ketones and oxygen in heterocycles. After extraction separation, infrared spectra showed reduced alcohol and methoxy groups, no ketones and some quinoid groups. Furan nuclei were condensed with aromatics, while methyl and alicyclic methylene groups were weakened. When separated with an aqueous-methanol solution of caustic soda, increased hydrated structures were found. Thin-layer chromatography, infrared, ultraviolet and mass spectra were used to determine the structures of 41 different components of the coal tar, showing its high-molecular polyfunctional nature with molecules of 2-5 condensed aromatic, naphthene, oxygen- and nitrogen-containing heterocyclic rings with phenol, alcohol, quinoid, methoxy and methyl substituents. Figures 3; references 20: 16 Russian, 4 Western.
[376-12131]

RHEOLOGIC PROPERTIES OF HYDRATED AEROSIL DISPERSION IN AROMATIC HYDROCARBONS

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR, SERIYA B: GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 7, Jul 83
(manuscript received 1 Apr 83) pp 38-41

KRUGLITSKIY, N. N., MAKAROV, A. S., ANDREYEVA, I. A. and SUSHKO, V. A.,
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[Abstract] Structural, mechanical and deformational characteristics of colloidal systems depend on physical-chemical properties of dispersion media such as polarity, dielectric permeability and solvating ability E_t . In an attempt to explain the effect of these indices on rheological properties of gels, the following systems were investigated: liquid phase of gels consisting of cumene, chlorobenzene, nitrobenzene and formamide; the solid phase consisted of hydrated aerosil with specific surface area of 200 m²/g. It was established that when E_t of these systems was 209-250 kJ/mole, sufficient for the formation of hydrogen bonding between the surface hydroxyl groups of aerosil and the molecules of the dispersion medium, an interaction between the solid particles

occurred through the solvate interlayer of the liquid medium. A direct particle-particle autoadhesion contact takes place when E_t is less than 125 kJ/mole. In the 125-196 kJ/mole range of E_t , when there is not enough energy for the formation of hydrogen bonding, both types of interaction take place. Figure 1; references 5 (Russian). [384-7813]

UDC 546.621

CRYSTALLINE STRUCTURE OF EuFe_2Al_8

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR, SERIYA B: GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 7, Jul 83 (manuscript received 22 Feb 83) pp 41-42

MANYAKO, N. V., STETS', I. N., KAVICH, Y. V., ZARECHNYUK, O. S. and YANSON, T. I., Lvov State University

[Abstract] During investigation of an isothermal section diagram of the system Eu-Fe-Al a new compound was noted with the composition EuFe_2Al_8 , for which now a more precise crystalline structure was determined using powder x-ray spectroscopy. The valence of europium was determined by the X-ray L-absorption spectroscopy; the simple form of L_{III} -adsorption edge showed it to be a bivalent element. Figure 1; references 5: 4 Russian, 1 Western. [384-7813]

UDC 546.47 + 546.268.6'39

REACTION OF METALLIC ZINC WITH NONAQUEOUS SOLUTIONS OF AMMONIUM THIOCYANATE

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR, SERIYA B: GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 7, Jul 83 (manuscript received 22 Feb 82) pp 47-49

PAVLENKO, V. A., corresponding member of UkSSR Academy of Sciences, SKOPENKO, V. V. and KOKOZEY, V. N., Kiev State University

[Abstract] Experimental results are reported on the reaction of zinc powder with nonaqueous (methanol, ethanol, propanol, acetone, acetonitrile, dimethylsulfoxide and dimethylformamide) solutions of ammonium thiocyanate. The reaction is spontaneous upon exposure to air in the reaction vessel. All of these solvents led to the formation of a single compound: $\text{Zn}(\text{NCS})_2(\text{NH}_3)_2$ in yields ranging from 72 to 94%. IR spectra and thermal stability of this compound are reported. Figures 2; references 9: 8 Russian, 1 Western. [384-7813]

ANIONIC COORDINATION COMPOUNDS OF LANTHANIDES WITH OCTAMETHYLMIDODIPHOSPHOTETRAMIDE

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR, SERIYA B: GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 7, Jul 83
(manuscript received 31 Mar 83) pp 51-53

TRYASHIN, A. S. and KOSOV, Yu. V., Kiev State University

[Abstract] Continuing their studies of lanthanides containing bis-phosphoryl ligands, the authors synthesized octamethylmidodiphosphotetramide (OMDP) and studied its reactions with lanthanoid salts. Reaction of NaOMDP with rare earth chlorides (LnCl_3) in methanol, followed by n-hexane extraction gave neutral complexes $\text{Ln}(\text{OMDP})_3$. Combining 1:1 ratios of $\text{Ln}(\text{OMDP})_3$ with NaOMDP in n-propanol gave $\text{Na}[\text{Ln}(\text{OMDP})_4]$, where Ln = Ce, Pr, Nd, Sm, Gd, Dy and Ho. Elemental analysis and data from IR and X-ray spectra indicated that the combination number for lanthanoid elements in these compounds was eight. References 5: 1 Russian, 4 Western.
[384-7813]

UDC 539.192

CALCULATION OF HEATS OF FORMATION AND OPTIMUM GEOMETRIC CONFIGURATIONS OF H_2O_3 AND H_2O_4 BY MINDO/3 METHOD

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 8, Aug 83
(manuscript received 10 Mar 82) pp 1910-1913

KHADZHI-OGLY, M. R., GLORIOZOV, I. P., YAGODOVSKAYA, T. V. and NEKRASOV, L. I., Chemical Faculty, Moscow State University imeni M. V. Lomonosov

[Abstract] Quantum chemical calculations were made of the heats of formation (ΔH_f°) of planar and nonplanar H_2O_3 and H_2O_4 molecules by the MINDO/3 method (Baird, NC, et al., J. Chem. Phys., 50(3):1262, 1969). In the case of H_2O_3 the difference in the heats of formation of the planar and nonplanar molecules was ca. 6 kcal/mole, indicating that both geometric configurations are equally probable. The difference in the case of H_2O_4 was 13.5 kcal/mole with a more pronounced minimum for the nonplanar configuration, indicating the greater probability of the nonplanar configuration with a dihedral angle close to 90° . The configurational data obtained by the MINDO/3 method appear to be more reliable than those derived by the EHT, CNDO/2 or ab initio approaches. Figures 2; references 8: 4 Russian, 4 Western.
[401-12172]

STUDY OF POLYAMIDOIMIDES AS CHROMATOGRAPHIC PHASES

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR:SERIYA KHIMICHESKAYA
in Russian No 4, Jul-Aug 83 (manuscript received 14 Jan 82) pp 43-50

ARKHIPOVA, I. A., ZHUBANOV, B. A., KIM, L. V., MASHKEVICH, S. A. and KAN, I. I.,
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[Abstract] New chromatographic sorbents consisting of an inorganic highly-porous carrier and a polyamidoimide coating on a base of trimellitimidic acids and alkylenediamines were produced and studied. Use of the sorbents to separate and identify products of oxidation and oxidative ammonolysis of acenaphthene, 4-bromoacenaphthene, pseudocumene and durol showed them to be effective in separating high-boiling, oxygen-containing and nitrogen-containing compounds. It was found that the selectivity of the sorbent is determined by the chemical structure and melting point of the polymer phase. Figures 4; references 10 (Russian).

[381-2791]

UDC 547.82

CERTAIN PHYSICOCHEMICAL PROPERTIES OF N,N'-PHENYL(α -PYRIDYL)THIOUREA

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 5 May 82) pp 1460-1466

USATENKO, Yu. I., MESHCHERYAKOVA, N. R. and PEDAN, V. I.

[Abstract] N,N'-phenyl(α -pyridyl)thiourea (I) is a bidentate ligand that, in addition to complex formation and use in the analysis of Pd, Pt, Rh and Ir, is also a potential herbicide and may possess therapeutic value. In view of its varied use in chemistry and biology, detailed characterization was conducted on aqueous solutions of I, involving an analysis of the UV spectra, determination of protonization and dissociation constants, and spectrophotometric analysis. The IR and NMR spectra of I were compared with those for diphenylthiourea in order to correlate spectra data with functional groups. Tabular and graphical representations of the findings are provided. Figures 5; references 12: 7 Russian, 5 Western.

[395-12172]

BIOCHEMISTRY

SYNTHESIS OF 5-S-CYSTEAMINE-6-HYDROXYTHYMINE AND PROOF OF ITS FORMATION UPON γ -RADIOLYSIS OF AQUEOUS THYMINE AND CYSTEAMINE SOLUTIONS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 8, Aug 83 (manuscript received 4 Aug 82) pp 1762-1768

GRACHEV, S. A., KROPACHEV, Ye. V. and LITVYAKOVA, G. I., Leningrad Institute of Nuclear Physics imeni B. P. Konstantinov, USSR Academy of Sciences, Gatchina

[Abstract] A study was made of the synthesis of 5-S-cysteamine-6-hydroxythymine RST and its identification upon radiolysis of solutions containing cysteamine and thymine. In a typical experiment, 2 ml of the solution being studied was added to 3 ml of a 0.2 M acetate buffer pH 4.5 containing 2,2'-dipyridyldisulfide at 10^{-3} M. Optical density was measured at $29,000\text{ cm}^{-1}$ 10 minutes after mixing of the reagents. The coefficient of molar extinction of thyropyridone liberated upon reaction of cysteamine with 2,2'-dipyridyldisulfide was taken as $8080\text{ l/mol}\cdot\text{cm}$. The compounds were separated by descending chromatography on Whatman-3 paper using methanol-concentrated HCl-water 7:2:1 or isopropanol-AcOH-water 6:3:1. Hydrolysis of 5-bromo-6-hydroxythymine at pH 5.5-7.5 was found to be a first order reaction with the formation of HBr and 5,6-dihydroxythymine. As the pH was varied from 5.8 to 7.6, the hydrolysis rate constant increased from $3\cdot 10^{-3}$ to $12\cdot 10^{-3}\text{ s}^{-1}$. Reaction of 5-bromo-6-hydroxythymine with cysteamine produces 5-S-cysteamine-6-hydroxythymine. Radiolysis of aqueous solutions of thymine and cysteamine forms cross linking products, one of which is identified as 5-S-cysteamine-6-hydroxythymine. Figures 6; references 17: 2 Russian, 15 Western.

[408-6508]

CATALYSIS

UDC: 541.128

USE OF FACTOR PLANS AND MATHEMATICAL-STATISTICAL PROCESSING OF QUANTUM CHEMICAL CALCULATION RESULTS IN PREDICTION OF CATALYTIC ACTIVITY

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 5 Nov 81) pp 811-818

GAGARIN, S. G., Institute of Fossil Fuels, Moscow

[Abstract] The purpose of this work is further development of calculation methods for prediction of catalytic activity, utilizing one of the advantages of these methods over purely experimental correlation approaches--the possibility of independent selection in calculations of the energy and spatial characteristics of active centers based on so-called factor plans. Calculations are based on the assumption that a catalyst should activate reagents such that the electron density in them corresponds as closely as possible to the distribution in the end product. The factor plan implemented in 16 calculations of both the multiplet and the di- σ -form determines unbiased estimates of the primary effects of all variables as well as estimates of a number of paired interactions in regression equations. The quantum chemical calculations performed with variation of the parameters on the basis of the factor plans can produce rich materials concerning the systems studied. Independent variation of electron and geometric characteristics of the active centers forming the electron state of the adsorbate allows determination of the peculiarities of the spectral manifestations of adsorption systems and their catalytic transformations. Figures 3; references 20: 16 Russian, 4 Western.
[407-6508]

UDC 339.192.194;535.33

USE OF X_α SCATTERED WAVE METHOD TO ANALYZE ELECTRON STRUCTURE OF CATALYSTS OF HYDROGENIZATION PROCESSES AND SELECTIVE HYDROGENIZATION OF UNSATURATED COMPOUNDS, PART 3: MODELING OF ELECTRON STRUCTURE OF ALUMINOPALLADIUM CATALYST

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 16 Dec 81) pp 819-826

GAGARIN, S. G., GUBSKIY, A. L., KOVTUN, A. P., KRICHKO, A. A. and SACHENKO, V. P.
Institute of Fossil Fuels, Moscow; Rostov State University

[Abstract] Results are presented from a detailed analysis of the interaction of PB atoms with a carrier based on calculation by the method of X_α -scattered

waves [See earlier reports of these authors, 1977, 1979, 1982]. Clusters of aluminum oxides in which the acceptor level located at the top of the valent band is not populated as a result of a shortage of aluminum cations are analyzed as models of symmetry clusters. The results indicate that the X_α -scattered wave method is reliable for description of the electron structure of both the carrier and the carried metals. The method allows the details of the complete set of electron characteristics of the carrier and the metal applied to the carrier to be determined at a level which is near quantitative. This allows extensive theoretical interpretation of experimental data and prediction of new catalysts. Figures 3; references 17: 15 Russian, 2 Western. [407-6508]

UDC 541.128

INFLUENCE OF CHEMICAL COMPOSITION OF OXIDE CATALYSTS ON DEHYDRATION RATE OF ISOBUTYL ALCOHOL AND COMPOSITION OF PRODUCTS FORMED

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 4 Aug 80) pp 877-882

KOTSARENKO, N. S. and MALYSHEVA, L. V., Institute of Catalysis, Siberian Division, USSR Academy of Sciences, Novosibirsk

[Abstract] This work studies the influence of the acid properties of catalyst surfaces on the dehydration rate of isobutyl alcohol and the composition of the products formed. The skeletal isomerization of isobutylene is also studied in order to determine means of formation of normal butylenes. The catalysts used were binary compounds of the type $aM_mO_n \cdot (1-a) SiO_2$, where $M=Al, Ga, Zr, Be$ or Y , and the oxides were SiO_2, Al_2O_3 . The rate of skeletal isomerization of isobutylene was determined from the quantity of n-butenes formed per hour per gram of catalyst. The rate of dehydration of alcohol was determined from the quantity of butenes liberated per hour per gram of catalyst. It was found that when proton acid centers were present on the surface of the catalysts, dehydration of isobutyl alcohol occurred by a carbonium-ion mechanism with very rapid formation of normal olefins. A change in the force of the centers leads to a change in reaction rate, but the same intermediate complex is formed. The reaction of dehydration of isobutyl alcohol is suggested as a test for the presence of proton centers on the surface of a catalyst. There are also aprotic acid centers on the surface of the catalysts studied. Their relative strength is rated. It is concluded that a change in the strength of the aprotic center should be reflected in the rate of conversion of the molecules. References 13: 9 Russian, 4 Western. [407-6508]

CATALYTIC ACTIVITY OF APPLIED MOLYBDENUM CATALYSTS IN OXIDATIVE DEHYDROGENATION OF n-BUTANE

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 1 Oct 80; after correction 31 Aug 82) pp 883-886

DOROSHENKO, V. A., SHAPOVALOVA, L. P., ZELENINA, A. I., TMENOV, D. N.,
TARANUKHA, O. M. and LUSHNIK, I. S., Petrochemistry Sector, Institute of
Physical-Organic Chemistry and Carbon Chemistry, Ukrainian SSR Academy of
Sciences, Kiev

[Abstract] A study is made of the specifics of catalytic action of the Mg-Mo system in the reaction of oxidative dehydrogenation of n-butane. Catalysts with various quantities of molybdenum applied to the surface were prepared by saturation of magnesium oxide with high specific surface with a solution of p-ammonium molybdate of the proper concentration and subsequent drying and heating in a current of air. X-ray structural analysis of the catalysts produced was performed on a diffractometer in CuK_α radiation. Additional information on the structure of the catalysts applied, normal magnesium molybdate and oxides of magnesium and molybdenum is presented in the form of IR spectra. Comparison of x-ray spectral and IR data with specific surfaces shows that the formation of the magnesium molybdate phase leads initially to a significant increase in the surface in comparison with the initial MgO . Further increases in the concentration of MgMoO_4 cause a decrease in specific surface. This is probably related to the processes of crystallization of the specimens. The variation in intensity of the EPR signal of the Mo^{5+} ion per unit of surface as a function of the content of molybdenum shows a maximum at 35-37 wt.% Mo. The number of active centers apparently increases in proportion to the content of the active MgMoO_4 phase on the surface up to a certain limit. Figures 3; references 16: 12 Russian, 4 Western.
[407-6508]

DETERMINATION OF EVAPORATION RATE OF WATER FROM PHOSPHORIC ACID CATALYST BY CHANGE OF CATALYTIC ACTIVITY

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 12 Feb 81) pp 887-889

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[Abstract] The purpose of this work was to study certain kinetic regularities of the evaporation of water from a phosphoric acid catalyst obtained by application of phosphoric acid to fused quartz. The rate of evaporation of water from the catalyst was studied with H_3PO_4 concentration in aqueous solution

71-77/5, ass %. Most of the experiments were performed at 90°C. Data on the kinetics of dehydration of tertiary butyl alcohol under the conditions of the pulsed chromatographic method were used to solve the problem. As water is introduced there is an initial reduction in k_{ef} of dehydration of tert-butyl alcohol to a minimum, after which k_{ef} increases to the value for the initial acid. The decrease in k_{ef} can be explained by dilution of the H_3PO_4 by the absorbed water. The minimum point is thought to be the point of completion of passage of the water impulse through the reactor. The subsequent increase in k_{ef} results from evaporation of the water in excess of the 77.5% H_3PO_4 , i.e., a decrease in the partial pressure of water in the reactor until the water vapor pressure equals the pressure imparted by the carrier gas. When the minimum value of catalytic activity is reached, a significant portion of the water is not absorbed and is carried out of the reactor. The quantities of water entering the gas and liquid phase are presented in a table and the method of calculation of the values is outlined. Figures 2; references 6: 5 Russian, 1 Western.
[407-6508]

UDC 541.128:546.719:547.313.3

CATALYSTS PRODUCED BY INTERACTION OF ORGANOMETALLIC TRANSITION ELEMENT COMPOUNDS WITH SURFACE OF OXIDE CARRIERS, PART 2: METATHESIS OF PROPYLENE ON RHENIUM CATALYSTS

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 18 Oct 81) pp 926-930

DANILYUK, A. F., KUZNETSOV, V. L. and YERMAKOV, Yu. I., Institute of Catalysis, Siberian Branch, USSR Academy of Sciences, Novosibirsk

[Abstract] A study is made of the catalytic activity of the system obtained by applying $Re_2(CO)_{10}$ to $\gamma-Al_2O_3$ in the reaction of propylene metathesis. The catalysts do not have significant activity in their initial state, but rather must be activated by heat treatment. The catalytic properties of specimens oxidized at 873 K as well as NH_4ReO_4/Al_2O_3 catalysts activated by the traditional method of oxidation at 873 K with subsequent heating in nitrogen at 829 K were similar. Studies of the catalysts showed that their catalytic activity varies significantly with a variation in processing conditions. The most active specimens were produced by reduction with hydrogen at 523 K after oxidation in oxygen at 773 K and by low temperature (300 K) adsorption of oxygen after reduction of the system NH_4ReO_4/Al_2O_3 by hydrogen at 773 K or decomposition of carbonyl rhenium in hydrogen or a vacuum at 773 K. The results of the studies indicate that catalytic centers of two different types may be formed. The first type is formed after reduction by hydrogen and these centers are stable up to 373 K or higher. The existence of an optimum temperature for reduction of oxidized catalysts indicates that rhenium ions with a certain moderate degree of oxidation are necessary for occurrence of the reaction catalyzed. Figures 4; references 14: 6 Russian, 8 Western.
[407-6508]

INFLUENCE OF WATER VAPOR ON CATALYTIC ACTIVITY OF POLYSULFOPHENYLENE
HYDROQUINONE ION EXCHANGE RESIN

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 29 Dec 81) pp 1002-1005

VINNIK, M. I., OBRAZTSOV, P. A., LIOGON'KIY, B. I. and BRIKENSHTEYN, A. A.,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] The reaction of dehydration of aliphatic alcohols in the presence of sulfocationites is studied by a pulsed gas chromatographic method. The experiment was conducted so that the catalytic activity of the resin was maintained constant throughout the experiment. This was done by maintaining a constant water vapor pressure in the installation by blowing the carrier gas through a bubbler at a preset temperature. The cationite powder was contained in a quartz tube 0.9 cm in diameter and 7 cm in length. The reagent tert-butyl alcohol was injected in pulses of 0.5 μ l into the reactor by a syringe. It was found that at constant temperature the catalytic activity of polysulfophenyl hydroquinone passes through a maximum when plotted against equilibrium water pressure in the gas phase. This apparently results from a change in the structure of the cation exchange resin--an expansion of the pores and an increase in the accessibility of the sulfogroups to the initial reagent. This effect has not been observed with other resins. This phenomenon is interesting from the standpoint of the possibility of varying the catalytic activity of resins and studying the physical and chemical properties of sulfocationites. References 14: 5 Russian, 9 Western.
[407-6508]

INFLUENCE OF DILUENT ON CATALYTIC CONVERSIONS OF 1,1-DIPHENYLETHYLENE ON
 γ -Al₂O₃

Moscow KINETIKA I KATALIZ in Russian Vol 24, No 4, Jul-Aug 83
(manuscript received 9 Mar 82) pp 1005-1007

BYKOV, V. I., RYABOV, V. D. and KOROBKOV, V. Yu., Moscow Institute of
Petrochemical and Gas Industry imeni I. M. Gubkin

[Abstract] A study is made of the influence of the nature of the diluent on the transformation of 1,1-diphenylethylene to determine the possibility of setting up the process of producing stilbene on a commercial scale. Experiments were performed in a continuous flow installation with a stationary layer of catalysts in an ideal extraction reactor at atmospheric pressure. The products of the conversion were analyzed by gas-liquid chromatography, chromatomass spectrometry and IR spectrometry. It was found that the conversion of 1,1-diphenylethylene depends to a great extent on the nature of the diluent.

The yield of stilbene is practically independent of the nature of the diluent, whereas the yield of 9-methylfluorine and 1,1-diphenylethane varies significantly. These yields are practically stationary with catalyst operation for 8 to 15 minutes. The significant increase in the yield of 9-methylfluorine and 1,1-diphenylethane when the reaction is performed in a current of hydrogen in comparison to nitrogen or water vapor, probably results from the formation of proton centers on the surface of the $\gamma\text{-Al}_2\text{O}_3$. References 5: 3 Russian, 2 Western.
[407-6508]

UDC 541.127+541.128

TRANSFORMATION OF CO_2 ON PALLADIUM-RUTHENIUM MEMBRANE CATALYSTS WITH NICKEL COATING CONTAINING LANTHANUM

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 26, No 7, Jul 83 (manuscript received 26 Oct 81) pp 882-883

SEROV, Yu. M., GUL'YANOVA, S. G. and GRYAZNOV, V. M., Department of Physical and Colloid Chemistry, Friendship of Peoples University imeni P. Lumumba

[Abstract] The purpose of this work was to study the influence of the introduction of lanthanum to the composition of a nickel coating, on the surface of a palladium-ruthenium membrane catalyst on the rate of formation of CH_4 and CO_2 . Experiments were performed at atmospheric pressure in a flow-through catalytic installation with an $\text{H}_2:\text{CO}_2$ ratio in the reaction zone of 4:1.

Nickel and lanthanum were applied to the surface of a palladium alloy foil containing 10% ruthenium from a nickel chloride-lanthanum chloride solution containing 40 g/l Ni^{2+} , 30 g/l La^{3+} and 20 g/l NH_4Cl . The introduction of lanthanum to the nickel layer increased the rate of formation of CH_4 from CO in the temperature range 573 to 663 K. From 573 to 683 K, the rate of formation of methane is increased though with further increases in temperature irreversible changes in the coating and a sharp decrease in the yield of CH_4 occur. Figures 2; references 4: 3 Russian, 1 Western.
[409-6508]

ELECTRON MICROSCOPE ANALYSIS OF PALLADIUM AND PALLADIUM-COPPER CATALYSTS ON ALUMINUM OXIDE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 36, No 7, Jul 83
(manuscript received 15 Apr 82) pp 430-433

GRIGORYAN, A. Sh., ISRAYELYAN, V. R., AYKAZYAN, A. M. and MAILYAN, N. V.,
Yerevan Polytechnical Institute imeni K. Marks; Armenian Institute of
Construction and Architecture, Yerevan

[Abstract] An electron microscope analysis was performed of palladium and palladium-copper catalysts on aluminum oxide to check the assumption that the addition of copper up to 30 at.% would have a diluting effect on the palladium, increasing the active surface of the palladium and thus increasing the catalytic activity. The electron microscope analysis was performed with a method of replicas and suspensions to study the form of precipitation of the metals on the carrier surface. Photomicrographs of the catalyst surface and diffraction pictures of the catalysts are presented. The results show that the precipitated metals form crystalline accumulations on individual portions of the carrier surface. When small quantities of copper (10 at.%) are added, the catalyst forms more dispersed metal particles. The diluting effect of copper is stronger if the rate of precipitation of copper from the joint solution is greater than the precipitation rate of palladium. If large quantities of copper (equal to palladium) are added, there is more interaction between palladium and copper and the catalytic activity decreases rather than increases. Figures 2; references 3 (Russian).
[405-6508]

REDUCTION OF APPLIED TUNGSTEN-CONTAINING CATALYSTS WITH ATOMIC HYDROGEN

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 8,
Aug 83 (manuscript received 10 Jan 83) pp 1715-1719

KLIMCHUK, Ye. G., SHELIMOV, B. N. and KAZANSKIY, V. B., Institute of Organic
Chemistry imeni N. B. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] A study was made of the possibility of formation of surface silico-tungstic acid by treatment of tungsten silicate catalysts with water vapor, using atomic hydrogen to reduce the catalyst. Specimens of tungsten silicate catalysts containing W(VI) 1.9% were dried at 343 K and heated for two hours at 773 K. Subsequent treatment was by evacuation at 300 K, heating in O_2 , evacuation, cooling to 424 K and withdrawal of O_2 or by admission of saturated water vapor at 300 K after heating in O_2 , evacuation, admission of O_2 , cooling to 424 K and evacuation of O_2 and holding for a certain period of time with

subsequent evacuation to 10^{-4} torr. The capability to be reduced by atomic hydrogen is characteristic apparently only of catalysts on whose surface the silicotungstic acid exists. Reduction with atomic hydrogen forms tungsten (V), which is easily oxidized by oxygen at 300 K and water vapor at 573 K. Figure 1; references 12: 8 Russian, 4 Western. [408-6508]

UDC 541.13;541.128.5:546.98

ELECTROCHEMICAL REGENERATION OF PALLADIUM CATALYSTS POISONED BY SULFUR

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 8, Aug 83
(manuscript received 22 Mar 82) pp 1942-1946

SUTYAGINA, A. A. and PEREPELITSA, V. A., Chemical Faculty, Moscow State University imeni M. V. Lomonosov

[Abstract] Studies were conducted on several approaches to electrochemical regeneration of palladium catalysts poisoned by sulfur in 0.1 N sulfuric acid.

^{35}S -labeled thiourea was employed as the poisoning agent under previously defined conditions. The results showed that the highest degree of sulfur removal (90-98%) was achieved by repetitious treatment of the electrode catalyst with positive potentials of 0.09-1.5 volts corresponding to maximum oxidation currents and sulfur desorption. Even better results (96-98%) were obtained by a combination of positive potential application and saturation of the palladium with hydrogen, and satisfactory results were also seen with anode-cathode polarization with a 10 mA/cm² current. The need for cyclical or repetitious cathodal polarization promotes reduction of PdS_2 to Pd-S_{abs}

particles and Pd-SH , which are then oxidized in the region of anodal potentials. Figures 1; references 13: 8 Russian, 5 Western. [401-12172]

UDC 621.039.8+541.128

ISOTOPIC OXYGEN EXCHANGE ON PALLADIUM CATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 8, Aug 83
(manuscript received 30 Mar 82) pp 1947-1950

KRAVCHUK, L. S., BESCHETVERTNAYA, T. I., NOVORODSKIY, B. G., NOVIKOVA, M. G., ZARETSKIY, M. V. and VALIYEVA, S. V., Institute of Physicoorganic Chemistry, Belorussian SSR Academy of Sciences, Minsk

[Abstract] Studies were conducted on heteromolecular isotopic oxygen exchange on unreduced palladium catalysts which differed in the metal content. The method of oxygen thermodesorption demonstrated that the palladium applied to $\gamma\text{-Al}_2\text{O}_3$ exists in the oxidized state during exchange and the metal content

(dispersity) determined the strength of the Pd-O bond. Furthermore, a significant increase in the rate of exchange in samples with a Pd \geq 0.5 mass% can be due to the oxide's decomposition and corresponding dilution of the gas phase by the "light" oxygen, as well as to exchange with the oxygen of the PdO phase. Figures 4; references 9: 1 Bulgarian, 5 Russian, 3 Western.
[401-12172]

UDC 541.128

STRUCTURE, ADSORPTIVITY, AND ACTIVITY OF SKELETAL PLATINUM-NICKEL CATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 8, Aug 83
(manuscript received 11 Mar 82) pp 2068-2070

BARKOVSKIY, A. I., SEMENOVA, A. D. and VOVCHENKO, G. D., Chemical Faculty,
Moscow State University imeni M. V. Lomonosov

[Abstract] Roentgenographic and electron microscopic studies were conducted on skeletal platinum-nickel catalysts and correlated with their efficiency in electroreduction of acetone. The composition of the melts corresponded to the formula $Pt Ni_x Al_{1-x}$, with $x = 0, 0.1, 0.2, 0.4, 0.6, 0.8$ or 1.0 . A true alloy was obtained only in the case when the content of platinum was 60 atom%. The nature of acetone adsorption for all the composition was similar; however, the binary catalysts with 20 atom% Pt showed the greatest activity in the electroreduction of acetone. This may have been due to the fact that in this type of platinum-nickel system the atoms are arranged in an ordered manner. Figures 1; references 3: 2 Russian, 1 Western.
[401-12172]

UDC 546.11:542.97

MECHANISM OF THE REACTION OF C_5 AND C_6 -DEHYDROCYCLIZATION AND SKELETAL ISOMERIZATION OF HYDROCARBONS ON METAL-CONTAINING CATALYSTS

Moscow USPEKHI KHIMII in Russian Vol 52, No 7, Jul 83 pp 1108-1135

BRAGIN, O. V. and KRASAVIN, S. A., Institute of Organic Chemistry imeni
N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] Dehydrocyclization and isomerization of hydrocarbons are discussed for processes using metallic and oxidized catalysts in five sections. Catalytic conversions of alkanes and cyclopentanes on Pt-catalysts are shown to pass through an intermediate dehydration stage, with varying difficulty. Dehydroisomerization of cyclopentanes, alkane isomerization, hydrogenolysis of cyclopentanes and C_5 -dehydrocyclization of alkanes are traced through scholarly studies. Good catalysts are palladium, iridium and rhodium and its alloys. Study of isomerization and C_5 -dehydrocyclization of alkanes and

hydrogenolysis of cyclopentanes made on the example of neopentane has permitted the explanation of 1,3-diadsorption in the "Anderson mechanism." Kinetic investigations and study of hydrogen's effect on these reactions showed the accelerating or retarding effect of hydrogen, depending on experimental conditions and the catalyst used. A kinetic isotope effect was observed in the C_5 reaction of isooctane on Pt/C when hydrogen was replaced with deuterium. Effects of aluminum and platinum catalysts and the effect of metallic catalyst structure are summarized. Despite much research, scant information is available on the structure of catalytic centers and orbital positions of surface metal atoms, and other factors. New methods in physics promise to add to the body of knowledge. References 170: 68 Russian, 102 Western.
[379-12131]

UDC 541.128

HYDROGENATION OF PHENYLACETYLENE WITH A RANEY Pt CATALYST FROM Pt-Cu ALLOYS

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA
in Russian No 4, Jul-Aug 83 (manuscript received 28 Jan 83) pp 16-20

KUZORA, T. V. and FASMAN, A. B., Institute of Organic Catalysis and
Electrochemistry, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Activity and selectivity of Raney catalysts, prepared from Pt--Cu alloys were studied during variation of the platinum level from 1 to 25 at. percent, using hydrogenation of phenylacetylene at 20°C, 30°C and 40°C in 90 percent alcohol as a model. The activity and selectivity of the Raney Pt in the phenylacetylene hydrogenation reaction depended on the chemical nature of the base component of the initial alloy. The high activity of catalysts from diluted alloys was due to their high dispersion. The lower selectivity of catalysts from alloys with a high Pt level was thought to be due to diffusion processes. The apparent magnitude of the energy of activation of the phenylacetylene hydrogenation reaction changed with a change in composition of the initial alloy. Figures 2; references 13: 11 Russian, 2 Western.
[381-2781]

UDC 541.124:547.56.04

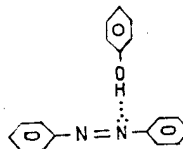
STUDY OF COMPLEX FORMATION OF AZOBENZENE WITH PHENOL, ANILINE AND MALEIC ANHYDRIDE

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA
in Russian No 4, Jul-Aug 83 (manuscript received 2 Dec 82) pp 20-24

ZHUBANOV, B. A., BOYKO, G. I. and KUDAYKULOVA, S. K., Institute of Chemical
Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Complex formation of azobenzene with phenol, aniline and maleic anhydride was studied by cryoscopic titration and infra-red spectroscopy

methods with use of model compounds; instability constants were calculated and the composition of the complex compounds was determined. Calculation of the concentration of components of azobenzene, maleic acid and phenol as a function of factors of association showed that factors of association of phenol and maleic anhydride increase with a decrease of concentration of the substances. Cryoscopic measurements showed that azobenzene in benzene interacts slightly with aniline but not at all with maleic anhydride. Maleic anhydride did not react with phenol or azobenzene separately. Complex formation of azobenzene with phenol changed the reaction capacity of the anhydride component. Analysis of infra-red spectra of the complex system and its components showed that, during complex formation of phenol with azobenzene, the absorption band of the monomeric form of the OH-group of the phenol is reduced while a new absorption band appeared ($3250-3480\text{ cm}^{-1}$) which may be related to the OH-group of phenol associated with the azobenzene. The results of cryoscopic and infra-red spectroscopy studies and analysis of data from the literature concerning protonation of azobenzene by mineral acids showed the structure of the complex to be:



Figures 4; references 8 (Russian).
[381-2791]

UDC 541.128:547.442.8:661.183.12

HIGH-MOLECULAR WEIGHT CATALYSTS IN ORGANIC SYNTHESIS, PART 5: CATALYTIC PROPERTIES OF POLYMERIC AMINOPROPANESULFONIC ACIDS

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA
in Russian No 4, Jul-Aug 83 (manuscript received 18 Oct 82) pp 483-486

ZITSMANIS, A. Kh. and ZILNIYETSE, I., All-Union Scientific Research Institute for Applied Biochemistry; "Biokhimreaktiv" Scientific Production Association

[Abstract] Continuing earlier studies of polymeric aminopropanesulfonic acids, the authors compared the catalytic properties of PAPS with those of other high-molecular weight catalysts in reactions such as the condensation of benzaldehyde with ethylcyanoacetate, which leads to ethyl-3-phenyl-3-cyanopropenoate. Spectrophotometric measurements were especially effective in following this procedure since the solvents used were transparent and the initial ingredients did not absorb significantly. The test acids proved to be effective catalysts only when their ratio of uncharged amino groups to aminopropane-sulfonic groups approached 1; under those conditions yield was more than 75% in a polar aprotic solvent at $80-100^{\circ}\text{C}$. Figures 4; references 4 (Russian).
[400-12131]

HIGH-MOLECULAR WEIGHT CATALYSTS IN ORGANIC SYNTHESIS, PART 6: IMIDAZOLES ON A POLYMER MATRIX

Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 83 (manuscript received 25 Nov 82) pp 487-491

ZITSMANIS, A. Kh., PAKULE, S. A., TETERE, G. G. and GRINSTEYN, V. Ya.,
Latvian University imeni P. Stuchka

[Abstract] Continuing their studies of high-molecular weight catalysts in organic synthesis, the authors describe the synthesis and catalytic properties of certain imidazoles on a polymer matrix produced by either alkylation of lithium imidazolide by a chloromethyl copolymer of styrene-divinylbenzene (CCSD) or of an imidazole and its derivatives by polyester tosylates. The test imidazoles were then used in affinic chromatography and as models of proteolytic enzymes. The alkylation took place readily in N,N-dimethylformamide as a medium and produced an imidazolyl-(1)-methyl copolymer of styrene-divinylbenzene after processing with an alkali. The product was a weak anionite; after further processing with alkylhalides, strongly basic anionites were obtained. The imidazole ring was not found to have pronounced catalytic action in condensation, but synthesized imidazoles on polymer matrices were good catalysts for other reactions. The catalytic action of related fluorides and hydroxides of [3-butylimidazolyl(1)-methyl copolymers was attributed to anion action rather than to action of the imidazole ring. Chemical procedures are summarized in the experimental section. References 23: 3 Russian, 20 Western.
[400-12131]

COAL GASIFICATION

UDC 662.741.3.022:622.765.001.5

PREPARATION METHODS OF COAL PULPS WITH REAGENTS PRIOR TO FLOTATION

Moscow KOKS I KHIMIYA in Russian No 8, Aug 83 pp 12-14

SOROKIN, A. F., FILIPPOV, A. I. and KOMAROVA, E. V., VUKhIN [Expansion unknown, possibly All-Union Scientific Research Institute of Coal Chemistry]

[Abstract] To increase the selectivity in the coal slurry enrichment process, conditions must be created under which floccule breakdown would take place during the preparation of the pulp designed to remove the particles with high ash content. This can be achieved by means of a vacuum or by addition of inert materials with exclusion of air; this breaks up the floccules formed and thus prevents their trapping of ash particles. Flotational experiments were performed under both conditions using magnetite and quartz powders. The results showed that conditioning of the pulp with reagents under conditions of air exclusion increased substantially the enrichment indices as compared to the process carried out in air. In either case a 5 min contact appeared to be the best. The process carried out with air exclusion was also more cost effective. Figures 3; references 5 (Russian)
[378-7813]

UDC 631.851:622-185/-188:622.749.2

POSSIBILITY OF UTILIZING NON-BLAST-FURNACE COKE FROM POORLY CLINKERING COAL FOR AGGLOMERATION OF PHOSPHORITES

Moscow KOKS I KHIMIYA in Russian No 8, Aug 83 pp 22-24

PUZANKOV, V. V., PEKHOTIN, G. A., ZOTEYEVA, A. A., BOCHAROVA, E. V., LESHCHENKO, B. P., OSIPOVA, V. M., TREFILOV, V. M., ANDRYUSHECHKINA, A. A., KOLESNIK, V. A., USTELEMOVA, L. I., GORDEYEVA, L. N., KHODYKIN, V. P. and GANINA, T. V., Volga Branch of Lenin Scientific Research Institute of Giprokhim [State Institute for the Planning of Plants of the Basic Chemical Industry]

[Abstract] One of possible substitutes for metallurgic coke for agglomeration of phosphorites is the non-blast-furnace coke from poorly clinkering coals. The present study was aimed at evaluating this approach. Experimental results showed that the quality of non-blast-furnace high and low ash content cokes from unenriched and enriched coal of Chernigov deposits is comparable to that

of metallurgic cokes with exception of ash content, insignificant yield of tarry substances, slight changes in ash composition and reactivity. These cokes can be used as fuels for agglomeration of phosphorite ore (small size) and as reducing agents of the phosphate crude in an electrothermal process. Taking into consideration easy enrichment of Chernigov coal and a number of technical and economical considerations, it is preferable to use the low ash content non-blast-furnace coke in production of yellow phosphorus. References 4 (Russian). [378-7813]

UDC 662.749.363.6:547.83(048)

SOME PROBLEMS IN RECOVERY AND PROCESSING OF HEAVY PYRIDINE BASES (REVIEW)

Moscow KOKS I KHIMIYA in Russian No 8, Aug 83 pp 24-30

NOVIKOV, Ye. G., VUKHIN [expansion unknown, possibly All-Union Scientific Research Institute of Coal Chemistry]

[Abstract] This is a review of pyridine recovery and its reactions. In the process of purification of various coal tar fractions, crude heavy pyridine bases (HPB) are obtained which are eventually subjected to fractional distillation. As a result, the only product obtained from this is quinoline. Because the extraction and processing of quinolines involve a number of operations which differ from plant to plant, an attempt was made to review them and to present the best approaches to this problem. Overall, however, a wide range of experimental approaches exists and all of them need a lot of improvement. Most of the optimal solutions were considered in a Japanese patent according to which the fractionation should be started at atmospheric pressure and completed in vacuum. This leads to separation of phenols in the forerun, leaving the azeotropic mixture of quinolines and residual phenols in the mother liquor. References 43: 19 Russian, 7 Polish, 17 Western. [378-7813]

UDC 662.749.363.62:547.83

IMPROVEMENT IN RECOVERY TECHNOLOGY FOR NITROGENOUS BASES FROM COAL TAR

Moscow KOKS I KHIMIYA in Russian No 8, Aug 83 pp 30-34

REPINA, Zh. I., VOROB'YEVA, L. A., KOSENKO, I. V., KOROLEVA, T. A. (Chernovtsy Metallurgical Plant) and GALANOV, M. E., Cherepovets Branch of North West Polytechnic Institute

[Abstract] The goal of this study was to find optimal conditions for production of heavy pyridine bases (HPB) containing maximum levels of quinoline from various fractions of coal tar. Prior to extraction of HPB the crude fraction

must be made free of phenolic substances, so as to minimize formation of neutral oils. Based on laboratory experiments, it was established that optimal conditions for extraction of HPB include: 20% H_2SO_4 for treatment of the tar fraction with a 1.1 fold excess; a 10 min time of contact followed by a 20 min sedimentation. This is not a single stage process and should be continued over and over until complete removal of pyridine bases. The HPB sulfates obtained should be neutralized with a 10% base used at a 1.1 fold excess. A method was reported in which neutralization of HPB sulfates could be performed directly in the tar processing section leading to a product containing 40% and more of quinoline. Figures 6; references 4 (Russian). [378-7813]

UDC 662.749.363.6

EFFECT OF PYRIDINE BASES IN CRUDE BENZENE ON ITS PROCESSING AND QUALITY OF PURE PRODUCTS

Moscow KOKS I KHIMIYA in Russian No 8, Aug 83 pp 34-36

CHAYSKIY, V. Ya., YEMEL'YANOVA, L. P. and TITUSHKIN, V. A., VUKhIN [Expansion unknown, possibly All-Union Scientific Research Institute of Coal Chemistry]

[Abstract] In one modification of the extraction of ammonia from coke gas, the base content in crude benzene increases substantially. Effect of this increase on sulfuric acid purification process was studied. In fact, it was shown that purification of benzene suffers, especially with high concentration of pyridine bases. This can be compensated for by using more sulfuric acid or by a more effective removal of pyridine bases, using 30-35% sulfuric acid, from the crude BTK fraction rather than from crude benzene. References 7: 4 Russian, 1 Polish, 2 Western. [378-7813]

UDC 543.544.45:662.749.33:547.82

GAS CHROMATOGRAPHIC DETERMINATION OF PYRIDINE PRODUCT COMPOSITION IN COAL

Moscow KOKS I KHIMIYA in Russian No 8, Aug 83 pp 36-41

NABIVACH, V. M., BERZILOV, Yu. S., DEGTYAREVA, L. V. [DKhTI -- expansion unknown, possibly, a (city) Chemical Engineering Institute], MARIICH, L. I. [UKhIN -- expansion unknown, possibly All-Union Scientific Research Institute of Coal Chemistry] and MARKUS, G. A., Phenol Plant

[Abstract] Coke-chemical industry produces many pyridine products from material extracted from coke gas. The analysis of pyridine bases on all of their preparatory stages is based primarily on gas-liquid chromatography for

which more than 50 solid phases have been developed, all with some deficiencies. Results obtained in this study tend to support the use of immobile liquid phase (poly-1,4-butanediolsuccinate or polyethyleneglycoladipinate) deposited over 1% trisodium phosphate carrier. Using this system it is possible to determine accurately individual components in all of the commercial products: pure pyridine, pyridine solvent, α -picoline, β -picoline and 2,4-lutidinic fractions as well as the crude starting bases. Figures 6; references 15: 10 Russian, 3 Czech, 2 Western.
[378-7813]

UDC 552.57

KINETICS OF OXIDATION OF NATURAL COALS BY ATMOSPHERIC OXYGEN

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 3 Dec 81) pp 52-55

SHANINA, Ye. L., ROGINSKIY, V. A. and MILLER, V. B., Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] To further knowledge about the mechanism of coal oxidation, the present study was aimed at learning the kinetics of oxidation absorption with reference to temperature, degree of pulverization, oxidation time, etc. The size of coal particles in suspension ranged from 0.05 to 0.1 mm, and temperatures from 50 to 150°C were used in various parts of the experiments. Results showed that the oxidation rate declined with increased duration, as the effective energy of coal oxidation activation also fell. This was attributed to both formation of a blocking oxidized coating and enrichment of the surface layer. Heating in a vacuum brought accelerated oxidation; e.g., the oxidation rate above 100°C was 2.3 times that at 80°C. Various oxidation inhibitors, such as tri-tert-butylphenol, ionol and phenyl-beta-naphthylamine, were applied either by heating in a vacuum or by application in a benzene solution to coal powder. These had no significant effect. A Warburg-type capillary manometer was found to be accurate in measuring the results of these tests and determining the likelihood of spontaneous combustion for various types of coal. Figures 3; references 10: 9 Russian, 1 Western.

UDC 552.574.22:542.943

OXIDATION PRODUCTS OF MOSCOW-AREA BOGHEAD COAL

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 22 Dec 81) pp 56-59

BAZAROVA, O. V., YEGOR'KOV, A. N., FOKIN, V. V., DZUMEDZEY, N. V. and KUCHER, R. V., Institute of Physico-Organic Chemistry and Coal Chemistry, USSR Academy of Sciences; Leningrad Technological Institute imeni Lensovet

[Abstract] Although sapropelite coals have received less scholarly attention than humus coals, they are promising raw materials for the chemical industry.

The current study was devoted to oxidation processes of boghead coals from the Seredeyskaya mine (Tulaugol' Production Association) in the Moscow area, [Podmoskovskiy lignite basin] with samples used having the composition W-3.4% (by weight), A-19.3%, C-57.7%, H-6.3% and S-2.5%. Oxidation was conducted in a continuous autoclave with 200 ml capacity under previously utilized conditions, in a 2.5% solution of caustic soda at 180°C. Yield, composition and distribution of carbon produced indicated that as much as 43.6% of the carbon in the initial boghead could be recovered for use, with other hydrocarbons being nearly completely reduced to volatile and soluble products. Esterification and subsequent gas-chromatographic analysis showed the cyclic nature of the organic substance in the boghead coal as well as the presence of aromatic rings. Figures 2; references 13 (Russian).
[376-12131]

UDC 662.74:66.094.17

ROLE OF MINERAL COMPONENTS IN PROCESS OF CATALYTIC COAL LIQUEFICATION

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 24 Sep 81) pp 75-77

ZEKEL', L. A., KRASNOBAYEVA, N. V., PCHELINA, D. P., TITOVA, T. A. and SHPIRT, M. Ya., Institute of Combustible Minerals

[Abstract] In previous studies of the effects of mineral components on coal liquefaction, hydrogenation was conducted without catalysts. The authors used ammonium paramolybdate and a sulfate of trivalent iron to hydrogenate brown coal of the Irsha-Borodino deposit in the Kansk-Achinsk basin, with 71.38% C, 4.4% H, 0.76% N, 0.19% S, 6.3%A, 1.1% W and 46.1% V. A steeping method was used to apply the catalysts to the coal. Hydrogenation results showed that the deepest conversion and yield of liquid products came with iron oxide catalysts, such as pyrite. Sodium carbonate and silicon oxide catalysts had no appreciable effect on the depth of conversion, but gave 10% lower yields of liquid products and 10% more gaseous products. Addition of ash from Moscow-area coals had a positive effect on conversion where iron, nickel or vanadium compounds were present, and a negative impact when aluminum, alkaline or alkaline-earth metals or arsenic were present. References 9: 3 Russian, 6 Western.
[376-12131]

STUDY OF ACTIVITY OF WIDE-PORE Co-Mo-CATALYSTS IN HYDROPURIFICATION OF COAL DISTILLATES

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 30 Mar 82) pp 78-83

KRICHKO, A. A., MALOLETNEV, A. S., YULIN, M. K., ARIFULIN, A. S.,
ZAYDMAN, N. M. and MILOVA, L. P., Institute of Combustible Minerals

[Abstract] Coal distillates intended to fill the need for liquid fuels are being developed in the USSR using the Kansk-Achinsk brown coal deposit because of low sulfur and ash content. Preliminary purification is required if such synthetic fuels are to be made into jet aviation fuel. The Institute of Combustible Minerals is employing Co(Ni)-Mo catalysts for this purpose, in the hope of eliminating nitrogen compounds as well as sulfur, oxygen and unsaturated hydrocarbons. The porous structure was found to have major importance in the effectiveness of such purification. Wide-pore aluminum oxide was used as a catalytic carrier at temperatures of 120-230°C, and the liquid hydrogenate came from Irsha-Borodino brown coal. Good purification was achieved using 1.1-1.7% hydrogen with insignificant gas formation (0.6-2.8%). Elimination of sulfur, nitrogen, oxygen, unsaturated compounds and nitrogen bases was 95, 92, 100, 97 and 100% respectively with the optimum of 11.0-12.0% MoO and 2.5-2.7% CoO, with porosity at more than 1000 Å. Figures 2; references 11: 10 Russian, 1 Western.
[376-12131]

EFFECT OF K_2CO_3 ADDITIVES ON BROWN COAL GASIFICATION

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 8 Jul 81) pp 84-86

SVIRIDA, L. V., MARKINA, M. S. and APUKHTINA, L. S., Moscow Chemical Technology Institute

[Abstract] The Kansk-Achinsk basin is regarded as the most favorable deposit of coal for energy and home gasification use. Since low-temperature conducting plasma used in power plants involves the additive K_2CO_3 , the present study was devoted to assessing that additive's effect on the reactive capacity of Kansk-Achinsk coal and the reactions of fuel carbon with carbon dioxide. After roasting at 800°C for 2 hours, various concentrations of K_2CO_3 were applied. Particle size in the range of 0.5-3.0 mm had no effect on reaction rate. Thus the reaction was attributed to purely kinetic features. Concentrations of up to 10% were found to have a beneficial impact on the coal gasification process. Figures 2; references 2 (Russian).
[376-12131]

ELECTROCHEMISTRY

UDC 541.13.133

ELECTRICAL CONDUCTIVITY OF SOLID ELECTROLYTE RbCu_2Cl_3 IN TEMPERATURE RANGE FROM 100 to 400 K

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 7, Jul 83
(manuscript received 19 Nov 81, after revision 10 Sep 82) pp 942-944

SHVETSOV, V. S. and VYBORONOV, V. F., Novocherkassk Polytechnic Institute
imeni Sergo Ordzhonikidze

[Abstract] Electrical conductivity of the solid electrolyte RbCu_2Cl_3 was studied at lower temperatures (from 100 K to 400 K as opposed to 293 K to 413 K) than had been attempted previously in order to observe possible phase transitions of electrical conductivity of RbCu_2Cl_3 . Plotting experimental data calculated by the equation $\sigma T = 4.4 \pm 0.4 \cdot 10^3 \exp[-0.204 \pm 0.003(\text{eV})/kT]$ produced approximately a straight line in the region of high temperatures but there was gradual deviation from this straight line in proportion to the decrease of temperature, probably due to deterioration of the grains of the pressed solid electrolyte. This can reduce the values of electrical conductivity at low temperature and can cause the hysteresis seen in cycles of cooling and heating of the sample. Jumps and breaks in electroconductivity as a function of temperature were not observed within the limits of accuracy of measurements, suggesting that the solid electrolyte RbCu_2Cl_3 does not undergo phase transitions in the 100 K to 400 K temperature interval. Figures 2; references 2 (Russian).
[383-2791]

UDC 541.138.3:547.752

ELECTROSYNTHESIS OF 2-METHYLINDOLINE

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 7, Jul 83
(manuscript received 29 Dec 81; after revision 23 Jul 82) pp 944-946

KRASNOSEL'SKIY, V. N., STEBLINA, Ye. I. and PONOMAREVA, L. A., Scientific
Research Institute of Organic Intermediates and Dyes, Rubezhnoye Branch

[Abstract] A study of electrochemical reduction of a sulfuric solution of 2-methylindol in an electrochemical cell without separation of the anodic and

cathodic spaces showed that the rate of conversion of the initial 2-methylindol depends upon the cathode material. Low yields of 2-methylindoline were obtained on platinum and copper electrodes having a low overvoltage of isolation of hydrogen; non-reacting 2-methylindol remained in solution. Complete reduction of 2-methylindol was not obtained at low current densities. It was found that, during electrochemical reduction of 2-methylindol, there is obtained 2-methylindoline with a yield of 90-95 percent for substance and 80-88 percent for current in a 54 percent solution of sulfuric acid, containing 10 percent 2-methylindol at current density of 2.5A/dm^2 and temperature of reaction 50°C . Figures 2; references 6: 4 Russian, 2 Western.
[383-2791]

UDC 621.357

ELECTROCHEMICAL METALLOINORGANIC POLYMER COATINGS

Moscow ELEKTROKIMIYA in Russian Vol 19, No 7, Jul 83
(manuscript received 5 Jan 82; revised 10 Sep 82) pp 949-950

KHABIBULLIN, I. G. and USMANOV, R. A., Kazan Chemico-technological Institute imeni S. M. Kirov

[Abstract] Infra-red spectroscopic study showed that high-melting particles are included in a coating with a hydroxylated surface while hydroxides forming at specific pH in the space around the cathode were unchanged in the coating. Behavior of particles in nickel sulfate solutions on the surface of aluminum oxide or silicon oxide particles at different pH were studied. Adsorption of nickel ions occurred directly on the particle surface at high pH; at low pH, fewer nickel ions were adsorbed on the aluminum oxide surface and, on the silicon oxide surface, water was adsorbed first and then nickel ions. The bond of nickel ions with the aluminum oxide surface was stronger than that with the surface of silicon oxide particles. Particles were included in the coating in different quantities according to their nature and structure. Radiospectroscopic studies of adsorption of copper ions on aluminum oxide particles and silicon oxide particles revealed no copper ions on the surface of the particles; electrodeposition showed their absence in the coatings. Introduction of chelating agents into the suspension revealed copper ions on particle surfaces. References 4 (Russian)
[383-2791]

NEW ROTATING ELECTRODE WITH TWO 'SANDWICH'-TYPE WORKING PARTS

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 7, Jul 83
(manuscript received 18 Jan 82; revised 7 Jul 82) pp 955-957

DOMAREV, A. N., KUMANTSOV, V. I. and SOSONKIN, I. M., All-Union Scientific Research and Design Institute of Monomers, Tula

[Abstract] A new rotating "sandwich" type electrode with the two working elements situated vertically are described, discussed and illustrated. The use of this device established experimentally, for the first time, that movement of a liquid in a diffusion layer proceeds upward from below--as opposed to existing ideas. This electrode can be used for more detailed study of mass transfer processes around a rotating cylinder. Figures 3; references 10: 7 Russian, 3 Western.
[383-2791]

KINETICS OF ELECTROCHEMICAL REDUCTION OF POTASSIUM FERRICYANIDE (III) ON UMV-30 CARBON MONOFIBERS, OBTAINED AT DIFFERENT TEMPERATURES

Moscow ELEKTROKHIMIYA in Russian Vol 19, No 7, Jul 83
(manuscript received 1 Jun 82) pp 966-968

MUNTYANU, G. G., Institute of Chemistry, MSSR Academy of Sciences, Kishinev

[Abstract] The effect of the end temperature of thermal processing of UMV-30 carbon monofiber on kinetics of electro chemical reduction of potassium ferricyanide (III) was studied by using 30 μ m thick monofiber containing 99.8 percent carbon and having a glass-carbon structure. The observed decrease of the rate constant of the reaction of electroreduction of potassium ferricyanide to UMV-30 carbon monofiber with the increase of the heat treatment temperature occurred because of the roughness of its surface. Values of rate constants of this same electrode reaction with use of other carbon materials were presented and compared with values for UMV-30. High temperature monofibers have the least surface roughness and therefore they have advantages over other carbon materials used as indicator electrodes since, in them, background currents depending on the surface roughness of the electrode are minimal. Figure 1; references 10: 2 Russian, 8 Western.
[383-2791]

ELECTROLYTIC DISSOCIATION OF WATER MOLECULES IN BIPOLAR ION EXCHANGE MEMBRANES

Moscow ELEKTROKIMIYA in Russian Vol 19, No 7, Jul 83
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[Abstract] Some aspects of previous studies of electrolytic dissociation of water with formation of H^+ and OH^- ions were reviewed briefly and a further study of the process of electrolytic dissociation of water molecules in MB-1, MB-2 and MB-3 bipolar membranes in a temperature range from 25°C to 55°C with change of the external electrolyte from 0.01 N to 0.5 N was described. Voltampere characteristics of bipolar ion exchange MB-3 and MB-2 membranes as a function of the concentration of the external electrolyte NaOH-HCl in semi-logarithmic coordinates were plotted and discussed. Electrolytic parameters for MB-1 membranes in NaCl and NaOH-HCl solutions at different concentrations and parameters for MB-2 and MB-3 membranes in solutions of NaOH-HCl at 25°C were tabulated and discussed with numerous allusions to the literature cited. References 8: 5 Russian, 3 Western.
[383-2791]

FERTILIZERS

CHEMICALIZATION OF THE ECONOMY OF CEMA COUNTRIES AND SOCIALIST ECONOMICAL INTEGRATION

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[Text] In this article, the level and different types of chemicalization of the national economy in countries of socialist collaboration are examined. The question is posed concerning the environment in connection with the development of chemical industry and the expansion of the use of chemicals in various spheres of economy and everyday life. Special attention is given to the role of chemistry in solving the problem of production. Several recommendations for perfecting collaboration of CEMA countries in the field of chemicalization of their national economies are given in this article.

In the past decade, chemicalization of national economies has become an important trend in the modern scientific technical revolution in countries of socialist collaboration. This has been made possible by the vigorous growth of chemical production, the development of principally new methods of producing materials and the introduction of chemical methods of reprocessing into many fields of industry and agriculture.

The significance of chemicalization in the expansion of the raw material base of industry in CEMA countries is great. Several artificial materials such as chemical fibers, synthetic rubber and others are being used due to the necessity of replacing natural raw material, because the possibility of obtaining it is limited. Other similar materials, plastics in particular, expanding the raw material base of industry and construction, are simultaneously reducing the amount of material employed in production and are increasing the time periods manufactured goods are of service. For many European CEMA countries, the use of plastics, moreover, to a great extent makes up for the shortage of several natural materials.

The replacement of several materials, especially metals, by plastics in machine building and construction in the future may lead to a substantial economy of energy resources, in so far as the energy output for the production and reprocessing of metals is higher than for plastics.

All-round chemicalization of agricultural production will actively promote the provision of a rational norm of feeding, first of all by virtue of the increase of farming productivity and the growth of livestock breeding productivity. The value of chemicalization also rises in providing demands of the population for widely used goods, expanding their assortment and improving their quality.

An increase in the level of chemicalization in all spheres of the national economy can also favorably affect the solution to the problem of the labor resource shortage, which the majority of CEMA countries have encountered. This ensues both from relatively low labor-intensiveness of the chemical production industry and in many cases from possibilities of reducing labor input when chemical materials are more widely employed.*

So wide is the area of the effect of chemicalization on various fields of economic life, that a natural question arises: how, specifically, is this direction of the scientific technical revolution reflected?

The majority of researchers believe that chemicalization of the national economy is formed from three components: the demand for chemical products in various spheres of the economy and people's lives; the introduction of chemical effect methods on materials in various fields of industry; and, the accelerated development of chemical industry itself (see 2,3).

However, the definition of the concept "chemicalization level" is by far not simple: for its characterization, the most varied indicators are used which reflect, depending upon the goals of research, any one of the directions of chemicalization.**

In our opinion, development rates of all three of the indicated components are reflected in the chemicalization level, and therefore it must be considered as a sum of indicators which characterize each of them.

*For example, the manufacture of parts from metal is 3-8 times more labor-intensive than the production of similar parts from plastic. In agriculture, a wider use of herbicides allows the number of mechanical processes to be reduced to the minimum, which is especially important in so far as the question of reducing labor-intensiveness of agricultural production stands out more sharply.

**Most often, indicators are used of the demand for chemical products both in industry and in everyday life. Less often they proceed from characteristics of the extent to which chemical reprocessing methods are introduced into production. For example, one can judge how deeply chemical methods of reprocessing raw material have penetrated into the wood reprocessing industry in relation to volumes in the production of pilomaterials and veneer (mechanical processing methods) and pulp, paper, cardboard and woodboards (chemical-mechanical and chemical reprocessing methods), which amounted to, in 1980, in the PRB--0.8, in the HPR--0.6, in the GDR--0.4, in the SRR--1.2, in the USSR--2.7 and in the CSSR--1.2 (calculated according to [5, p 105-107]). Thus, in spite of the great extent of production output with the use of mechanical processing methods, the GDR is distinguished by the highest level of chemicalization of the wood reprocessing industry.

In addition, the third component should be specially discussed--the level of chemical industry development. It has developed in CEMA countries at high rates which exceed world averages. This has secured an increase of the share of the region in world manufacture of chemical products from 18% in 1960 to 30% at the present (see [9, 1980, No 1, p 3]).

Large appropriations for the development of chemical and rubber-asbestos industry and quick growth rates, leading general industry indicators, has led to a marked increase of the relative share of production of this field in the total industrial production of all CEMA countries, which in 1980 was estimated to be, in the PRB--9.0%, in the HPR--13.2, in the GDR--10.6, in the PPR--9.4, in the SRR--9.0, in the USSR--7.6 and in the CSSR--8.5% (see [5, p 77]).

In the majority of CEMA countries, the chemical complex contains practically all sectors and sub-sectors of chemical production, the assortment of production released is widely diversified and the demand for the most important chemicals in the national economy has already reached extremely substantial indicators, which is indicated by the table (data for 1980).

Among CEMA countries, the first place according to the general level of chemicalization of the economy is occupied by the GDR, which also leads by all individual indicators (with the exception of the general volume of chemical production). This country has the most ramified and interlinked chemical complex; constant attention is given to reinforcing all of its sections.

The mass introduction of petroleum gas raw material in the middle of the 60's led to the creation of a series of large modern industries in the GDR (nitrogen, olefin chemistry), but by no means did this supplant traditional types of lignite raw material and syntheses based on it. In the modern stage, in connection with the short supply of liquid and gaseous hydrocarbon raw material, the manufacture of technological gases and hydrogen on the basis of solid fuel will again become one of the most important directions of the expansion of raw material base in chemical industry. The GDR, which has significant technical work in progress in the field of lignite gasification, possesses the most favorable prerequisites for the development and technical improvement of these methods. The expansion of lignite production to 290 million tons by 1985 will make it possible to provide both power engineering and the chemical industry raw material of native extraction to a greater degree than was the case in the 70's (see [11]).

However, according to the scale of entire chemical production, the GDR yields preeminence to industry in the SRR which developed vigorously in the 70's. According to overall volumes of the output of basic types of chemical production, the GDR and SRR are comparable at the present. According to per capita production, Rumania exceeded the GDR with such products as nitrogen and phosphorous fertilizers (107.8 kg/person, versus 78.5 kg/person) and sulfuric acid (79.1 kg/person versus 57.2 kg/person). According to the average per capita output of synthetic rubber, the GDR exceeds the SRR 1.4-fold.

Table. 1980 Indicators of Chemical Demand in CEMA Countries.

[N.B. The Russian text gives no heading for this table.]

Indicators	PRB	HPR	GDR	PPR	SRR	USSR	CSSR
Total use of most important chemical agents (fertilizers, agents for plant protection, plastics, chemical fibers, synthetic rubber, varnishes and paints and soda products) in per capita calculation, kg	202	230	261	172	135	136	253
Deliveries of mineral fertilizers for 1 hectare of plowed field and perennial plants, kg	205	262	325	244	113	84	334
Portion of chemical fibers in the use of textile raw material, %	55	45	68	52	56	30	50
Portion of synthetic detergents in the use of all detergents, %	25	40	85	25	22	41	36

Note: Calculated according to [5] and according to statistical manuals of CEMA countries.

In addition, with respect to total demand for the very important chemical products per capita (mineral fertilizers and methods of plant protection, synthetic rubber, plastics, chemical fibers, calcined and caustic soda, lacquers and paints, the GDR exceeds the SRR two-fold. The reason for this is that the developed chemical industry of Rumania until now has not been a basis of all-round chemicalization of the economy and a great degree of its production is exported out of the country (45% of fertilizers and soda, more than 35% rubber, 25% plastics and up to 20% of chemical fibers) (see [12; 5, p 7, 97-99, 382]). In comparison with the GDR, the material balance of the SSR is distinguished by a considerably less chemical volume. The lower efficacy of its production is also largely connected with this.

In the example of Rumania, it will become apparent that for any country's chemical industry to fulfill the role of one of the leading sections in an industrial and social rise, it is not enough to intensify accretion of production volumes only in this industry, but a proportional, balanced development for industry-consumers of the chemical products is also necessary.

The CSSR stands in second place according to the extent of chemicalization among CEMA countries; the demand for important chemicals there is close to the GDR's level. However, whereas the high level of chemicalization in the GDR is directly connected to the strength of its own chemical economy, in Czechoslovakia--in spite of the notable growth of this industry in the second half of the 70's--it is maintained to a considerable extent by the import of many chemicals.

The HPR is in third place among CEMA countries in chemicalization level, although, according to the extent of chemical production it occupies one of the last places. The consumption of chemicals in this country is almost 1.5-fold greater than internal production (see [13]). Hungary is especially clearly following a defined, selected line of development, even in the long-term not placing problems of satisfying demands in complete assortment at the expense of its own industry.

Altogether in CEMA countries, separate sectors of industry and agriculture differ very essentially with respect to the achieved level of chemicalization: from this point of view, they can be divided into three groups.

The first group encompasses those sectors and industries in which the consumption of chemical production has reached a high degree of saturation. This is the preparation of rubber tires, cable products, instruments, many items for household equipment and silk materials; in agriculture, the cultivation of industrial, vegetable and melon crops and corn.

Sectors and industry of the second group are characterized by potentially great possibilities of expanding chemicalization, and the proportionate consumption of chemical materials in them is significantly lower than technically and economically justified demands. This is the preparation of industrial rubber products in which a considerable amount of fabric from cotton fibers is used; the automobile industry; the production of polymeric construction materials; the wood-processing, furniture and other sectors of industry; a significant portion of the output of woolen fabrics and tricot and detergents; in agriculture--the cultivation of grain and fodder crops, and, also, animal husbandry.

The third group includes those sectors in which the chemicalization process has not yet appeared. This contains, in particular, several sectors of heavy machine building, construction, the fuel-energy industry and others.

In comparison to other main directions in the development of scientific technical progress--automation and electrification--the process of expansion and deepening of chemicalization has more limitations. The most important of them are negative sequelae of this process for the state of the environment. However, in the near future, chemical industry can quit playing the role of such a considerable polluter. In socialist countries, an essential portion from general capital investments into chemistry is deducted for environmental protection, expenditures on purification of discharges and atmospheric

emissions are increasing, the water recirculation factor is accelerating and reprocessing systems are introduced for chemical industry wastes which are considered as secondary material resources.*

Another aspect of chemicalization, namely the consumption of chemical products in spheres of the economy and everyday life, is, as yet, linked to a growing pollution of the environment and, first of all as the result of use of chemicals everywhere, far greater as compared to production territorially dispersed. For example, the utilization of polymeric packaging still remains an unsolved problem. Now, a significant portion of plastics goes for the production of packaging (in the HPR and PPR--more than 1/4 of all produced plastics, in the USSR--12% and in the SRR--60%) (see [14]). The solution to this problem, undoubtedly, requires common efforts from countries of socialist collaboration.

With all the undesirability of many consequences of chemicals in the economy and everyday life (the extent of their manifestation is quite varied in the different countries), chemization is still an inevitable, objective condition of the modern stage of development of productive forces. It makes a weighty contribution to solving problems of increasing production-effectiveness of the socialist countries.

In the process of equalizing levels of economic development in CEMA countries, a converging of the chemicalization levels of the national economy will occur. But, the type of chemicalization in the different countries will, most likely remain different: for some, the high chemicalization level will be, to a vital degree, connected with the development of the native chemical industry (GDR, SRR, PPR, USSR), and, for others, it will probably rest on essential imported supplement of chemical consumption (HPR, PRB, CSSR).

In solving the task of equalizing chemicalization levels while preserving its varied types, there is great significance in the development of the international socialist division of labor. And precisely in this field, very many problems arise which relate first of all to the choice of priority directions and the most acceptable forms of cooperation.

*This system of measures is conducted in all CEMA countries. However, the greatest interest is presented by the present experience of the GDR, where consultation service on the use of chemical products in the national economy is strengthened. Its most important task has become the provision of the most rational and economical usage of raw material and energy in the production of chemicals and especially a more complete use of secondary raw material. It is known that this not only reduces the harmful influence of chemical processes on the environment, but also decreases the cost of production and energy and material expenditure of industry. It is expected that the specific suggestions by the consultation service will render no small real effect. Thus, optimizing forms of packaging and employing secondary plastics for them will enable them to save approximately 5 thousand tons of plastics, the use of only secondary plastics for the protection of cables in construction will reduce the outlay of polyethylene of low density to 700 tons, etc. Favorably affecting the solution of ecological problems, these measures simultaneously lead to a rise in the degree of chemicalization (see [9, 1981, No 3, pp 20-22]).

A definite differentiation not only of types, but also, for the time being, of levels of chemicalization in CEMA countries determines a well-known difference in primary problems in the development of chemical complexes and, to a certain extent, hampers their common solution by several governments. But, at the same time, the objective tendency toward equalizing levels of chemical industry development in CEMA countries creates even more favorable conditions for deepening integration processes.

Under the influence of the scientific-technical revolution, systematic and profound structural, technological, organizational and other changes are taking place in chemical production itself. On this basis, definite grounds are increasing for the development of economic collaboration and the use of these or other forms of bringing about integration measures in relation to specific trends of technical progress.

The interrelationships of CEMA countries in the field of chemical industry which have arisen lately are characterized, on the whole, by a rather wide spectrum of directions and the presence, in a series of sub-sectors, of permanent contacts and traditions of collaboration.

International specialization and cooperation of production (ISCP) became a basic form of mutual contacts. The proportion of specialized production in the overall value of mutual export of chemical goods of CEMA countries rose from 12.0% in 1975 to 32.8% in 1980. In the PRB, the quota of specialized shipments in the export of chemical production in CEMA countries in 1980 was estimated at 20.3%, in the HPR--62.4%, in the GDR--27.3%, in the PPR--54.0%, in the USSR--20.9% and in the CSSR--42.5% (see [6]).

The share of specialized goods in mutual export has grown most essentially for such aspects of chemical production as organic dyes and semifinished products (from 45.3% in 1975 to 58.2% in 1980), motion picture materials (respectively 0.6 and 40.2%), chemical agents for plant protection (10.0 and 71.6%) and plastics and materials for their production (3.2 and 24.5%). Here, the highest indicators of specialization are for chemical industry and manufacturing which put out products designated for other non-chemical sectors. This is explained by many reasons. In particular, it is explained by the fact that the majority of them are related to sectors of low-tonnage chemistry in which optimum capacities as a rule exceed the demand of one country (with the exception of the USSR). This, to a certain extent, serves as a technological and economical basis for international specialization and cooperation. And nevertheless, ISCP is brought about first of all by the fact that demands for chemicalization anticipate possibilities of an increase of chemical industry of any country. In spite of the fact that the above-mentioned sectors of chemical industry exist in all countries, not one of the national chemical complexes is able to provide the wide assortment of production which is required for industry-consumers.

Therefore, today the overwhelming majority of operating multilateral agreements on the ISCP is related to production which is oriented toward providing chemicalization of the national economy, and not toward the development of chemical industry itself, and it is manifested in the form of an assortment exchange.

In bilateral interrelationships, these directions of ISCP also have become in essence a priority. Here they develop even more intensively by virtue of the greater flexibility of the mechanism of bilateral specialization in comparison to multilateral. Moreover, bilateral contacts allow collaboration to be adjusted according to a wider circle of industry sectors, including multiple-tonnage production. As an example, in the period from 1976 to 1980, the Polish chemical industry participated in the realization of five multilateral agreements and 20 bilateral pacts on the specialization of producing pharmaceutical drugs, plant protection agents, chemical agents, lacquer materials, industrial rubber products, synthetic rubber, fibers and production of the petrochemical industry. In accordance with protocols on coordination of plans for the development of the national economy for 1981-1985 between the USSR and PRB and the GDR and CSSR, specialization is being implemented in the field of intermediate products of chemical industry and pharmaceutical items, and between the USSR and SRR--in the production of chemical agents for plant protection, mineral fertilizers and other aspects of chemical production, etc.

However, until the present, neither increased development of the chemical industry, nor intensification of the mutual exchange--between CEMA countries--of this sector's production on the basis of ISCP, are yet in a position to completely satisfy the demand for chemicalization of the national economy in many directions. For example, agriculture does not satisfy the assortment of pesticides proposed by chemical industry of CEMA countries. In animal husbandry, there is a deficiency of such production as fodder yeasts, amino acids, vitamins and other fodder additives. As yet it is still not possible to provide a high level of chemicalization in sectors which demand the most important polymeric materials. CEMA countries produce 13.2% of the world output of plastics and synthetic resins and 15.8% of chemical fibers (1978), which is lower than their share in the total production in world chemical production (see [4]).

Main reasons for the marked lag of CEMA countries with respect to this progressive production group are concealed in the absence of necessary scientific projects in progress, the insufficient level of chemical machine building development, a number of unresolved problems of the raw material base of chemistry and the poor development of production of auxiliary substances. In some cases, industry-consumers are also technically not prepared for the inclusion of new chemical materials.

Therefore, it is correct to conclude that in the near future, it will be most important to achieve preeminent development of collaboration precisely in these industrial sectors, guaranteeing simultaneously their correlation and orientation to solution of those tasks of chemicalization of the national economy which are primary for all the countries.

This can be illustrated by the example of scientific technical collaboration in the field of chemistry. It has already been developing for 25 years, it encompasses the widest range of research and developments, but, nevertheless, it still does not sufficiently contribute to the solution of indicated problems.

In multilateral collaboration, the coordination of research conducted within the limits of scientific technical councils and industrial groups of the CEMA Permanent Commission for the Chemical Industry has remained a basic form for a long time. On this foundation, agreements were concluded in five of the most important fields of chemical production--plastics and synthetic resins, monomers for synthetic rubber, chemical fibers, chemical goods for consumers and pulp and paper production. More than 200 research and project design organizations of CEMA countries, which have completed 90-120 specific jobs yearly, participated in such a collaboration in 1976-1980. Special councils of delegates conduct the organization of the process of collaboration and observation of the course of program execution. However, in spite of such a large amount of work in the activity of delegate councils, only a few cases were mentioned when results of developments by partners were used: for example, the creation of a line of packaging for liquid detergents and joint recommendations on planning large-tonnage production of styrene.

The low degree of production assimilation of results of scientific technical collaboration is connected, in our opinion, first of all, to the insufficient preparation of a general mechanism of economic collaboration for uniting, jointly, the interrelationships in science and technology with the contacts in the production sphere. In the second place, selected themes of scientific technical cooperation by far do not always correspond to the most acute tasks of the development of chemical industry and to the most important goals of chemicalization of the national economy of the CEMA countries, which objectively reduces the interest of the separate countries in their industrial realization. Apparently, for this reason, only a third of the problems and themes of the plan for multilateral scientific-technical cooperation in the framework of CEMA in 1981-1985 is projected to be carried out on the basis of agreement relations (see [7, 1981, No 3, pp 88-90]). Consequently, only a third of all conducted works will be able to be assured the complex planning which encompasses the stage of scientific research, developments and production realization.

The further development of raw material and energy bases of the chemical industry of CEMA countries will become a complex scientific technical problem in our time. This results from the condition of supplies of basic types of chemical raw material, from the deepening location of their deposits and from the conversion to assimilation of almost inaccessible deposits. Therefore, problems of developing and introducing more effective methods and technology of both extracting raw materials and utilizing them are moving to the foreground. Simultaneously, the need for a reduction of the relative expenditure of raw material and energy in chemical industry sectors is increasing by virtue of the completion of technological solutions and the creation of non-waste or low-waste production.

Thus, future tasks of chemicalization of the national economy in CEMA countries require an essential reconstruction of the existing collaboration scheme. The transition to a complex examination of the entire problem is necessary, including collaboration in scientific technical developments, in production of corresponding equipment, in a search for opportunities for the most effective utilization of raw material and energy resources and in joint location of the most rational forms of dividing production programs.

The question of imparting a complex nature to collaboration in the development of progressive chemical productions in principle is not new: it had already been placed on the agenda in the early 70's. The complex program of economic integration of CEMA countries stipulates, for example, in the field of plastics, the development of an entire series of collaboration measures such as the use of already conducted research and project design jobs, joint designing and the installation by united forces of new capacities, specialization and cooperation of production, providing the necessary raw material and auxiliary materials on cooperating principles and also collaboration in reprocessing plastics into products (see [1]).

Much of this has been realized. At the same time, the incomplete implementation of set tasks is linked to the fact that specified measures were not coordinated into one system with an apportionment of corresponding resources: scientific-technical potentials, chemical machine building and the raw material base turned out to be insufficiently prepared.

A new stride in the business of providing the complex nature of collaboration in separate chemical industry sectors was completed upon development and acceptance of long-term purpose programs of collaboration (LPPC). Basically, the direction of collaboration in the future in the field of chemistry is defined by two programs: LPPC for guaranteeing economically-based demands of CEMA countries for fuel, raw material and energy and LPPC in the field of agriculture and the food industry.

A sub-program--which is related to chemical industry--of the first of these two LPPC's is based on the principle of utilizing raw material and energy resources of the USSR for the output of energy-intensive production with the goal of shipping it to other CEMA countries. In the Soviet Union, supplementary capacity for the production of ammonia, methanol, polyethylene, polyvinyl chloride and isoprene and polyvinyl rubber have been created. At the same time, in other European CEMA countries, enterprises will be constructed for providing the USSR with less energy and material-intensive production (polyurethane, synthetic dyes, epoxy resins, polycarbonates, chemical additives, agents for plant protection, textile auxiliary substances and others).

This second LPPC mentioned above aims efforts of chemists in CEMA countries at comprehensive chemicalization of agriculture. First of all, problems must be solved of satisfying demands of plant production for high quality mineral fertilizers and agents for plant protection, and of animal husbandry--for various fodder additives. Collaboration is foreseen in the creation of new types of highly concentrated, complex and compound fertilizers and the solution to problems of producing phosphorus fertilizers, and ISCP is projected for biochemical and chemical feed additives. In accordance with the General Agreement, the Mozyrskiy plant is being constructed in the USSR in collaboration with other CEMA countries, for the output of nutrient yeasts from highly purified petroleum liquid paraffins with a capacity of 300 thousand tons a year. These programs will become the basis of bilateral collaboration as early as the current Five-Year Plan. In accordance with the protocol on coordination of plans for the development of the national economy of the USSR and GDR for 1981-1985 and on the basis of the agreement on equal exchange of Soviet energy-intensive original chemical materials and semimanufactures for products of high

chemical development from the GDR in the period up to 1985, the GDR will be receiving from the Soviet Union ammonia, butadiene, methanol, low-pressure polyethylene, etc., sending the USSR in exchange emulsifiers, auxiliary substances for the production of plastics and dyes and polyurethane components (see [8]).

On the whole, the acceptance of the LPPC signalized a new stage in planning of economic collaboration for CEMA countries. The use of the method of program-purpose planning to the greatest extent responds to the nature of modern production and is able to more completely guarantee the realization of projected measures, in so far as along with the development of "purpose" production, a resource guarantee of their increase is also planned. However, tasks of chemical production entered into the indicated programs really only in their resource section, which was oriented to the realization of basic purpose units of each program, and they therefore turned out to be reduced according to a separate LPPC. The weakest link in the development of the chemical complex of CEMA countries--its material-technical base--was allotted an insignificant place. One cannot say that in the LPPC, the chemicalization problem found complex reflection.

Therefore, in our opinion, the question may be posed right now concerning the development in the future of a complex program of collaboration for CEMA countries in providing comprehensive chemicalization of their national economies.

The following could become basic elements of a program which would encompass not only the problem of developing industry, but also of utilizing chemical production:

- a single scientific technical policy;
- coordinated investment activity;
- a system of interconnected perspective measures aimed at the development of chemical machine building;
- a system of measures for solving the problem of providing raw material for chemical industry;
- coordination of actions in the field of marketing chemical production and its use in the national economy.

Such a complex program would issue from demands for chemicalization in the entire CEMA region. However, according to each element, it naturally could encompass only those directions where there is a real interest in the development of foreign economic relations.

Intentions for the realization of leading trends in chemicalization determine the necessity to construct programs as a combination of mutual agreement sub-programs of collaboration (each one of which would be composed of the same elements) with respect to separate industry sectors, for example, in chemicalization of agriculture, chemicalization of construction, chemicalization of sectors of light industry, etc. However, difficulties of an agreement on so wide a circle of questions, when there is insufficient preparation for this mechanism of collaboration, could become an essential hindrance in the development of such a program as a whole.

Therefore, at first it might be possible to attempt, as an experiment, to develop one of the sub-programs, for example, a complex program of collaboration in the field of chemicalization of agriculture.

Prerequisites for the development and joint realization of such a program are being created, first by the Food Program accepted in the USSR which presented enormous tasks for chemical industry; second, by the priority development of sectors of agricultural chemistry which was being planned in the 80's by all European CEMA countries.

In the Soviet Union, deliveries of mineral fertilizers to rural areas must by 1985, be brought up to 26.5 million tons of food-stuff, and, by 1990, to 30-32 million tons (in comparison to 19.2 million tons in 1981). Toward the end of the present Five-Year Plan, agriculture must receive 680 thousand tons of chemical agents for plant protection and, by 1990--750-790 thousand tons. Deliveries of preserved fodder must amount to no less than 110 thousand tons in 1985 and 380-400 thousand tons in 1990 (see [7, 1982, No 9, p 30]).

Improvement of the structure of the chemical complex of practically all CEMA countries anticipates the leading development of chemical production for agriculture. In 1981-1985, the PRB, with an approximate 1.4-fold increase of the scale of all chemical production, anticipates preferred (double) growth of the output of phosphorus fertilizers and production of microbiological industry. The volume of production of chemical agents for plant protection (pesticides) will increase 2.5-fold. Technical re-equipment is foreseen of a series of industries for the output of agricultural chemistry products and raw material for it. Powerful lines will be constructed for the production of ammonia with yearly productivity of 400 thousand tons and for the output of ammonium nitrate with a capacity of 450 thousand tons a year, carbamide production will be expanded (see [9, 1981, No 4, pp 8-10]).

In the chemical industry of the HPR in this Five-Year Plan, a primary rise in output of nitrogen fertilizers, carbamide and superphosphate will be secured. Among priority directions in the development of Hungarian chemistry which are planned by the centralized program for the period up to 1990, the most important place is occupied by production of agents for plant protection (3.5-fold increase in a decade) and intermediate products for their production (12.5-fold increase in the same time). In 1981-1985 alone there will be approximately 10 new enterprises constructed for the production of pesticides and 12 for the production of intermediate products. In this regard, possibilities will be created toward 1990, not only for the expansion of export of plant protection agents, but also for foreign trade deliveries of raw material for them (see [15]).

In the SSR in 1981-1985, the output of mineral fertilizers which will increase 2-2.5-fold will develop much faster in comparison with the entire chemical industry (see [10]).

New capacities for producing agricultural chemicals are expected to be put into operation in the CSSR.

Thus, programs planned for the period to 1985 and to 1990 on the development of chemical complexes of CEMA countries create a definite material stockpile for the joint development and execution of a complex program for chemicalization of agriculture. However, it cannot be limited to questions of interrelationships in the development of production of strictly chemicals for agriculture: fertilizers, pesticides, food additives and others. It would be necessary to include therein a number of important interconnected questions, such as solution to the problem of raw material base for production of mineral fertilizers, the possibility of collaboration in the construction of remote ammonia pipelines, which would allow for the concentration of power for production of ammonia near deposits of natural gas, and the organization in agriculture of the wide use of liquid ammonia. An important element of the program will be intensification of research in the field of producing new, more effective agents for plant protection. A composite part of it would be collaboration in the creation of a high-developed infrastructure of chemicalization of agriculture, including transport, production of packaging materials, construction of warehouses, means of mechanization of loading and unloading operations, fertilizer mixers, methods for chalking soils, procedures for applying mineral fertilizers and poison chemicals and agricultural-chemical stations and laboratories.

It is also possible to begin with an even narrower task, for example, with the development of a joint goal-directed program for chemicalization of animal husbandry. The selection of immediate trends in the development of such programs will be determined by the priority of industry sector demands in guaranteeing their chemicalization. Nevertheless, any one of them will be effective only in the case that they will be of an intersectorial nature, which advances new requirements for improvement of the entire mechanism of economic collaboration of CEMA countries.

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12473

CSO: 1841/375

NITROGEN COMPOUNDS

UDC 542.127/542.951.1

STUDY OF INTERACTION OF CARBOXYLIC ACIDS WITH AROMATIC AMINES

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA
TEKHOLOGIYA in Russian Vol 26, No 7, Jul 83 (manuscript received 16 Dec 81)
pp 794-798

MASLOSH, V. Z., CHASNYK, O. F., KUDYUKOV, Yu. P. and IGNATKINA, T. R.,
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[Abstract] Results are presented from a study of the reaction of amide formation on model systems: benzoic acid, stearic acid and amines--aniline, p-nitroaniline, p-toluidine, α -naphthylamine and α -aminoanthraquinone. The rate constants and activation parameters of the process are determined at 453-513 K. The acids and amines were reacted with the amines with a ratio of functional groups $\text{COOH}:\text{NH}_2=2:1$. The reactivity of stearic acid was higher than that of benzoic acid in amide formation with all of the amines studied. The change in rate constants with increasing temperature for all reactions of the acids follows Arrhenius equation, the activation energy varying from 44 kJ/mol for p-nitroaniline to 90 kJ/mol for p-toluidine. The rate constants were similar for both acids. Figures 3; references 10: 9 Russian, 1 Western.
[409-6508]

UDC 541.515:547.822.5

NITROXYL RADICAL WITH IODOETHYL GROUP

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 8,
Aug 83 (manuscript received 18 May 83) p 1933

AL'TMAN, I. B., ZHDANOV, R. I., KARDANOV, N. A., TRIYAONOVA, S. A.,
GODOVIKOV, N. N. and KABACHNIK, M. I., Institute of Heteroorganic Compounds
imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow; Scientific Research
Institute for Biological Testing of Chemical Compounds, Kupavna

[Abstract] The authors synthesized 4-(β -iodoethyl)-2,2,6,6-tetramethylpiperidine-1-oxyl (II) containing a β -iodoethyl group by the interaction of 4-(β -hydroxyethyl)-2,2,6,6-tetramethylpiperidine-1-oxyl with methyltriphenoxyphosphonium iodide. References 3: 2 Russian, 1 Western.
[408-6508]

ORGANOMETALLIC COMPOUNDS

UDC 547.77-546.23+546.22+539.21

ORGANIC METALS AND SUPERCONDUCTORS BASED ON DERIVATIVES OF TETRATHIOFULVALENE

Moscow USPEKHI KHIMII in Russian Vol 52, No 8, Aug 83 pp 1301-1325

LYUBOVSKAYA, R. N., Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka

[Abstract] Study of so-called organic metals has expanded greatly in the past 10 years, and many synthetic organic metals that have been produced behave like "real" metals at the same time that they display unusual electrical, magnetic and electronic properties. Ion-radical salts and charge-transfer complexes are two major categories of such metals that are described in the present survey, which is divided into sections on organic metals based on donor compounds, organic metals and superconductors based on derivatives of tetrathiofulvalene. The second section of this review summarizes developments with respect to unsubstituted tetrathiofulvalene and its compounds with inorganic anions, organic metals based on dibenzotetrathiofulvalene, organic metals and superconductors based on tetramethyltetraselenofulvalene, where superconductivity has been discovered in the past 3 years, organic metals based on tetramethyltetrathiofulvalene, especially at low temperatures, and organic metals based on bis-(ethylenedithiolo)tetrathiofulvalene. The author concludes that while properties from dielectric to superconductive features have been found, instability remains the greatest problem and greatest challenge for future research. Increased pressure that raises the level of three-dimensionality can bring the desired stability. References 150: 22 Russian, 128 Western.
[403-12131]

ELECTRIC SURFACE PHENOMENA IN THE PROCESS OF FLOTATION EXTRACTION OF TETRATHIOCYANOMERCURIATE IONS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 26, No 7, Jul 83 (manuscript received 21 Dec 81) pp 831-834

SKRYLEV, L. D., BULYGINA, L. M. and SIN'KOVA, L. A., Department of Physical Chemistry, Odessa State University imeni I. I. Mechnikov

[Abstract] This work is intended to determine the significance of electric surface-phenomena in the process of flotation separation of tetrathiocyanomercuriate ions $\text{Hg}(\text{SCN})_4^{2-}$ collected by means of alkylpyridinium hydrochlorides containing 10 to 16 carbon atoms in the alkyl portion. Experiments were performed with solutions of potassium tetrathiocyanomercuriate containing 45 mg/l mercury, obtained by the interaction of mercury nitrate and potassium thiocyanate in excess. The effectiveness of the collection agents increases with increasing alkylpyridinium hydrocarbon radical length in the pH areas near 3 and 10. The electrokinetic potential of the sublate particles is negative for collecting agent consumptions of not over 125% of the stoichiometric value necessary to bond all of the tetrathiocyanomercuriate ions in the solution, and is positive at greater rates of consumption. Figures 3; references 12 (Russian). [409-6508]

DECOMPOSITION MECHANISM OF ORGANIC METAL COMPOUNDS OF TRANSITION METALS AND ROLE OF INTERMEDIATE PARTICLES IN CATALYSIS

Moscow USPEKHI KHIMII in Russian Vol 52, No 7, Jul 83 pp 1086-1107

DOLGOPLOSK, B. A., Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences, Moscow

[Abstract] The present study reviews research on the decomposition of organic metal compounds from as far back as 1915, when saturated and unsaturated hydrocarbons corresponding to the alkyl groups of the initial RMgX were noted. Free radical stages were generally emphasized in early studies. Homolytic breaking of the C-M bond was observed for compounds with a weak C-M bond, while carbenes were observed as highly reactive particles in diazo-compounds. Experimental results of decomposition at the time of formation and ratios of alpha-disproportionation and recombination are presented for lithium and magnesium in compounds with Pt, Pd, Cr, Rh, Mo, Re, Ta, Nb and Co. A chain metathetic process influenced by carbene complexes involves compounds of Mo and W on Al_2O_3 , and the olefins that result form high-molecular polybutadiene.

Processes for producing cyclopentene and acetylene polymers are also discussed. Elementary catalytic conversions include hydrogenolysis and skeletal isomerization of hydrocarbons such as cyclopropane and derivatives, hydrocarbon dehydration and olefin hydration. Hydrogenolysis of the carbon skeleton was traced through dehydration (formation of a C=C bond), emergence of carbene complexes and attachment of hydrogen to them. Hydration involved a two-stage process of olefin attachment at the M-H bond and hydrogen at the C-M bond. References 108: 53 Russian, 55 Western.
[379-12131]

UDC 541.124+547.314+661.185.23.3

SYNTHESIS AND TRANSFORMATIONS OF TRIBUTYLPHOSPHINE ADDUCT WITH
PHENYLACETYLENE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 36, No 7, Jul 83
(manuscript received 12 Mar 82) pp 456-462

GASPARYAN, G. Ts., MINASYAN, G. G., TORGOMYAN, A. M., OVAKIMYAN, M. Zh. and
INDZHIKYAN, M. G., Institute of Organic Chemistry, Armenian SSR Academy of
Sciences, Yerevan

[Abstract] Studies show that tributylphosphine reacts with phenylacetylene at about 120°C to form a colored 1:1 adduct which may have the structure of phosphobetaine with a negative charge on the β -carbon atom or its isomer with the pentavalent phosphorus atom. The IR spectrum of the adduct has absorption bands at 1605, 1635, 3030, 3075, 3090 and 970 cm^{-1} . When an aqueous solution of hydrobromic acid is added to the adduct, the color disappears completely leading to a product corresponding to quaternary phosphonium salts formed from the betaines. Thin layer chromatography shows that the product formed is a mixture of two compounds, tributyl- α -phenylvinylphosphonium bromide, and tributyl- β -phenylvinylphosphonium bromide. References 7: 2 Russian, 5 Western. [405-6508]

UDC 542.91:547.1'118

INTERACTION OF SULFOCHLORIDES AND CHLOROPHOSPHATES WITH 1,3,2-
DIHETEROPHOSPHOLANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 8, Aug 83 (manuscript received 22 Nov 82) pp 1859-1863

PUDOVIK, M. A., OSTANINA, I. L. and PUDOVIK, A. N., Institute of Organic and
Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The reactions of carboxylic acid halides with cyclical amido-phosphites occur either at the P atom with the formation of phosphonium halides or products of Arbuzov regrouping, or at the endo- or exocyclic N atoms with breaking of the P-N bond. The authors of the present article attempted to find reactions which occur with breaking of the P-N bond and formation of P-S derivatives. The reactions of benzene sulfochloride with linear and cyclical

amido-derivatives of trivalent phosphorus are found to be accompanied by oxidation of the phosphorus atom. The reactions of trivalent phosphorus amides with diethylchlorophosphate occur with breaking of the P-N bond and lead to products of exchange of an amino group at the P atom for Cl. A number of diphosphorylated methylaminoethanol derivatives are synthesized and their thermal stability studied. References 10: 7 Russian, 3 Western.
[408-6508]

UDC 542.91:547.1'118

UNUSUAL REACTION OF DIETHYLAMINOMETHYL(METHYL)PHENYLPHOSPHINE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 8, Aug 83 (manuscript received 9 Feb 83) p 1926

ARBUZOV, B. A., YERASTOV, O. A. and NIKONOV, G. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The interaction of diethylaminomethyl(methyl)phenylphosphine (I) with isobutyl ester of diphenylboric acid in the presence of paraform yields 2,2,5-triphenyl-5-methyl-2-boronata-5-phosphonium-1,3-dioxane (II), the first example of substitution of an aminomethyl group by an oxymethyl group in tertiary phosphines. The formation of diethylmethylamine and isobutyric aldehyde indicates occurrence of hydride transfer from the isobutoxyl group to an aminomethyl group. References 2 (Russian).
[408-6508]

UDC 547.26'118

REACTION OF SUBSTITUTED METHYLENEAMIDOPHOSPHITES WITH α -HALOCARBONYL COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83 (manuscript received 13 Jul 82) pp 1471-1478

KONOVALOVA, I. V., BURNAYEVA, L. A., GAREYEV, R. D., LYAKHOVA, A. S., MOSHKINA, T. M. and PUDOVNIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Studies were conducted on the reaction of substituted methyleneamido-phosphites with various α -halocarbonyl compounds (aldehydes, ketones, esters and amides of carboxylic acids, etc.) which demonstrated that the reaction of the methyleneamidophosphites with chloral and chloroacetone follows the Perkow rearrangement with the formation of enol phosphates. Ethylchloroacetate reacts with N-(phenylmethoxymethylene)amidophosphite according to the Arbuzov reaction with the formation O-methyl- α -ethoxycarbonylmethyl-N-(phenylmethoxymethylene)amidophosphonate, while ethyltrichloroacetate yields both O-methyl- α -ethoxycarbonyl- β,β -dichloromethyl-N-(phenylmethoxymethylene)amido-phosphonate and O-methyl-O L - α -ethoxy- β,β -dichlorovinyl-N-(phenylmethoxymethylene)-amidophosphate. These reactions yield oxidation products with amides of

trichloroacetic acid. Reaction of α -chloroacetoacetic ester with N-(phenylmethoxymethylene)amidodimethylphosphite results in the formation of the E and Z isomers of O-methyl-O'-(1-ethoxycarbonyl-1-propen-2-yl)-N-(phenylmethoxymethylene)amidophosphate. Figures 1; references 8: 7 Russian, 1 Western. [395-12172]

UDC 547.26'118

REACTION OF DIALKYLISOCYANATOPHOSPHITES WITH ETHYL ACETOACETATE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 13 Jul 82) pp 1478-1483

KONOVALOVA, I. V., BURNAYEVA, L. A., GAREYEV, R. D., YARKOVA, E. G., KASHTANOVA, N. M., TEMNIKOVA, Ye. N. and PUDOVNIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Studies were conducted on the reaction of dimethyl- and diethylisocyanatophosphite with ethylacetoacetate in 1:1 ratio without solvent or in carbon tetrachloride for 7-10 h to yield a viscous liquid from which, by means of multiple vacuum distillations, were isolated dialkyl esters of 1-methyl-2-ethoxycarbonylvinyl, substituted 1,2-azaphospholane, and isocyanates of dialkylphosphoric acid. The products indicated that the dialkylisocyanatophosphites reacted with the enol form of ethyl acetoacetate as a result of a nucleophilic attack of the P atom on the electrophilic β -carbon of the C=C bond to form a bipolar ion, which was transformed into 1,2-azaphospholene with a P=N bond by ring closure. The latter is unstable and gives rise to the dialkyl esters and 1-alkyl-2-alkoxy-2,5-dioxo-3-hydroxy-3-methyl-4-ethoxycarbonyl-1,2-azaphospholane. The small amount of isocyanates of dialkylphosphoric acid presumably resulted from oxidation of the ketone form of ethyl acetoacetate. Further studies showed that reaction of dimethylphenylmethoxymethyleneamidophosphite with ethyl acetoacetate did not lead to a cycloaddition product, but that heating of the reagents (100-120°C) resulted in thermal isomerization of the phosphite into methyl phenylmethoxymethyleneamidomethylphosphonate. Figures 1; references 11: 9 Russian, 2 Western. [395-12172]

REACTION OF DIPHENYL(N,N-DIETHYLAMINOMETHYL)PHOSPHINE WITH TIN(4+) HALIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 22 Sep 82) pp 1483-1488

MURATOVA, A. A., YARKOVA, E. G., BURANGULOVA, R. N., SAFIULLINA, N. R.,
MOROZOVA, N. P., KHRAMOV, A. S. and PUDOVNIK, A. N., Kazan State University
imeni V. I. Ul'yanov-Lenin

[Abstract] Studies were conducted on the reaction mechanisms of diphenyl(N,N'-diethylaminomethyl)phosphine with SnCl_4 , SnBr_4 and CH_3SnCl_3 in pentane or methylene chloride under a dry inert gas, with phosphine: Sn compound ratios of 2:1 and 1:1. Spectroscopic and chemical analyses of the products demonstrated the formation of molecular complexes-- $[\text{Ph}_2\text{PCH}_2\text{Et}]_2\text{SnX}_4$ ($\text{X} = \text{Cl}$ or Br ; $n = 1$) -- in which the donor-acceptor bond involves an unshared electron pair of the phosphorus atom. These complexes undergo redox decomposition with subsequent rupture of the P-C bond in the P-C-N fragment and formation of dihalide(tetraphenyldiphosphine)stannate (2+) and bis(N,N'-diethyliminium)-hexahalostannate (4+). Figures 1; references 16: 3 Russian, 13 Western. [395-12172]

STRUCTURES OF COMPLEXES FORMED BETWEEN METHYL ALKYLPHOSPHONATE AND TIN HALIDES AND ALKYLHALIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 22 Sep 82) pp 1489-1493

MURATOVA, A. A., YARKOVA, E. G., MOROZOVA, N. P. and PUDOVNIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] IR and NMR studies were conducted on methyl esters of methyl- and ethylphosphonous acid which showed lack of rotation around the P-O-C bond, but revealed that methyl ethylphosphonate has free rotation around the P-C-C bond. Synthesis and studies were also conducted on the complexes that these esters formed with tin halides, alkylhalides and with TiCl_4 , giving $[(\text{CH}_3\text{O})\text{RP}(\text{O})\text{H}]_2(\text{CH}_3)_n\text{SnX}_{4-n}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}$; $n = 0, 1$) and $[(\text{CH}_3\text{O})\text{C}_2\text{H}_5\text{P}(\text{O})\text{H}]_2\text{TiCl}_4$ complexes, respectively, in which the donor-acceptor bond formation involved participation of unshared electron pair of the phosphoryl oxygen. $[(\text{CH}_3\text{O})\text{CH}_3\text{P}(\text{O})\text{H}]_2\text{SnX}_4$ ($\text{X} = \text{Cl}, \text{Br}$) complexes in the crystalline state have the cis-octahedral structure, and in solution the trans-octahedral conformation, while $[(\text{CH}_3\text{O})\text{RP}(\text{O})\text{H}]_2\text{CH}_3\text{SnX}_3$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}$) always retain the trans state. Figures 1; references 11: 10 Russian, 1 Western. [395-12172]

HYPOPHOSPHITE REACTIVITY, PART 6: REACTION OF HYPOPHOSPHOROUS ACID WITH ACETYLENE ALCOHOLS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 18 Oct 82) pp 1493-1503

BELAKHOV, V. V., YUDELEVICH, V. I., KOMAROV, Ye. V., IONIN, B. I.,
KOMAROV, V. Ya., ZAKHAROV, V. I., LEBEDEV, V. B. and PETROV, A. A., Leningrad
Technologic Institute imeni Lensovet

[Abstract] Detailed studies were conducted on the reaction mechanisms of hypophosphorous acid with acetylene alcohols (propargyl alcohol and dimethylethynylcarbinol), which resulted in the formation of allene phosphonites representing previously unstudied hydrophosphoryl compounds. The purpose of the investigation was also to uncover novel organophosphorus compounds that may have antibacterial activity. Reaction of the acid with the alcohols in benzene with azeotropic distillation led initially to the formation of propargyl phosphinites, which underwent hydrophosphoryl acetylene-allene rearrangement with simultaneous hypophosphite-phosphonous isomerization. Tabular and graphic data are presented for allene bond-containing phosphinates, including quantum calculations for the $C=C-C-P=O$ bonds. Figures 5; references 16: 12 Russian, 4 Western.
[395-12172]

EPOXIDATED ESTERS OF p-HALOPHENYLALKYLPHOSPHINIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 23 Jun 82) pp 1503-1509

LIORBER, B. G., TARZIVOLOVA, T. A., ZYKOVA, T. V. and RAZUMOV, A. I.,
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[Abstract] Details are presented on the synthesis of C-phosphorylated (I) and O-phosphorylated epoxides (II). The synthesis of II involved reaction of p-halophenylphosphonites with haloalkyls via Arbuzov rearrangement, and treatment of the p-halophenylalkylphosphinates with phosphorus pentachloride to yield chlorophosphinates. The latter were reacted with glycidol to give the glycidol p-halophenylalkylphosphinates. For the synthesis of I p-halophenylphosphonites were treated with allyl bromide and the resultant p-halophenylallylphosphinates were oxidized with peracetic acid to give esters of p-halophenyl- β,γ -epoxypropylphosphinous acids. Oxidation of the allyl-p-halophenylallylphosphinates led to the formation of the I and II diepoxides. Structural confirmation was obtained by IR, NMR, and PMR spectroscopies. Figures 1; references 6: 5 Russian, 1 Western.
[395-12172]

PHOSPHORYLATION OF HETEROCYCLIC COMPOUNDS, PART 3: REACTION OF PHOSPHORYLATED
2,2,2,5-TETRAPHENYL-3,4-DIAZA-1,2-OXAPHOSPHOL-4-ENE WITH NUCLEOPHILIC AGENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 24 Jul 82) pp 1509-1512

ZHMUROVA, I. N., YURCHENKO, V. G. and PINCHUK, A. M., Institute of Organic
Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Studies were conducted on the identification and reactivity of the intermediate products formed in the phosphorylation of 2,2,2,5-tetraphenyl-3,4-diaza-1,2-oxaphosphol-4-ene by the binary system $\text{Ph}_3\text{P}/\text{CCl}_4$ in triethylamine to 2,2,2,4-tetraphenyl-6-triphenylphosphonio-5,6-diaza-1,3,2-dioxaphosphorinane chloride. On the basis of NMR spectra the intermediate product was identified as an acyclic oxyphosphonium salt which reacts with aniline, p-toluidine, and p-chloranil via the carbonium electrophilic center to give triphenylphosphazine benzoic acid anilides. Reaction of the oxyphosphonium salt with hydrogen sulfide and p-nitroaniline via the phosphonium active site results in the removal of, respectively, triphenylphosphine thiooxide and triphenylphosphazo-p-nitrobenzene. References 6: 1 Russian, 5 Western.
[395-12172]

REDUCTION OF TETRAKIS(DIALKYLAMIDO)PHOSPHONIUM HALIDES BY SODIUM
IN LIQUID AMMONIA

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 24 Jul 82) pp 1513-1517

MARCHENKO, A. P., KOYDAN, G. N., POVOLOTSKIY, M. I. and PINCHUK, A. M.,
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[Abstract] Studies were conducted on the reduction of quasiphosphonium compounds by metallic sodium which demonstrated that reduction of symmetric substituted tetraamidophosphonium halides (I) by this metal in liquid ammonia led to the formation of triamidophosphites. The ease with which reduction occurred diminishes in the following sequence which coincides with the decrease in the solubility of I in liquid ammonia: $\text{CH}_3 > \text{C}_2\text{H}_5 > \text{C}_4\text{H}_7 > \text{C}_6\text{H}_9$. Reduction of asymmetric I yields both asymmetric and symmetric triamidophosphites, with the smaller alkyl radicals being split off preferentially. Furthermore, selectivity of the process increases as the temperature is lowered (-30 to -60°C). Involvement of the phosphoryl radical in the reduction of I is indicated by the fact that reduction of tetraamidophosphonium chlorides, containing easily removed benzene or phenylsulfonyl groups, leads to phosphazoalkane production with splitting of the N-C and N-S bonds. References 10: 6 Russian, 4 Western.
[395-12172]

REACTION OF α -OXYALKYLPHOSPHONATES WITH ALKYL- AND ARYLISO(THIO)CYANATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 27 Aug 82) pp 1517-1525

PROKOF'YEVA, A. F., GRYAZNOVA, L. P. and MEL'NIKOV, N. N., All-Union
Scientific Research Institute of Chemical Means of Plant Protection, Moscow

[Abstract] Studies were conducted on the chemical behavior of the oxy group of α -oxyalkylphosphonates (I) by reacting a number of I with alkyl- and aryliso(thio)cyanates as electrophilic reagents. IR and PMR spectroscopies demonstrated that the reaction of I with these chemicals gave rise to the corresponding phosphorylated carbamates. Alkylation of the resultant addition products with haloalkyl compounds involved the nitrogen atom in the case of products formed with the isocyanates to form N,N-disubstituted phosphorylated carbamates, and the sulfur atom in the isothiocyanate products to give phosphorylated S-alkyliminoesters. References 8: 4 Russian, 4 Western.
[395-12172]

REACTION OF 2-CHLORO-1,3,2-DIOXAPHOSPHOLANES AND -PHOSPHORINANES WITH 1,3-DIOXACYCLANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 5 Jul 82) pp 1525-1532

KRUTSKIY, L. N. (deceased), SAFIULINA, O. Z., KRUTSKAYA, L. V., CHERNYAK, Ye. I. and TSIVUNIN, V. S., Kuzbas Polytechnic Institute, Kemerovo

[Abstract] Studies were conducted on the effects of several substituents in the 2 position of dioxolane on the course of the Arbuzov rearrangement in the reduction of 2-chloro-1,3,2-dioxaphospholanes (I) and -phosphorinanes (II) with unsubstituted and substituted 1,3-dioxolanes and 1,3-dioxanes. The PMR and NMR data showed that rearrangement of the intermediate quasiphosphonium salt involved rupture of the 1,3,2-dioxaphosphocyclane ring. Reaction of I and II with 4-methyl-1,3-dioxolanes yielded a mixture of 2-(β - or γ -chloroalkoxy)-5- and -6-methyl-1,4,2-dioxaphosphorinanes. Reaction of 2-alkoxy-1,3,2-dioxaphosphorinanes with chloromethylalkyl ether involved ring rupture and formation of dialkyl alkoxymethylphosphonates. Figures 3; references 8 (Russian).
[395-12172]

REACTION KINETICS OF P(III) ACID ESTERS WITH 1,5-DIHYDROPERFLUOROPENTANAL HYDRATE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 11 Oct 82) pp 1537-1541

ALEYNIKOV, S. F., KRUTIKOV, V. I., MASLENNIKOV, I. G., KASHKIN, A. V. and
LAVRENT'YEV, A. N., Leningrad Technologic Institute imeni Lensovet

[Abstract] Standard methods were employed to study the reaction kinetics and thermodynamic parameters of the reaction of P(III) acid esters -- $RP(OR')_2$; where $R = C_2H_5, OCH_2CF_3, OCH_2(CF_2CF_2)_nH, n = 1-3$; $R' = CH_2CF_3, CH_2(CF_2CF_2)_nH, n = 1-3$ -- with 1,5-dihydroperfluoropentanal in the temperature range 10-100°C in benzene under inert gas. Evaluation of the thermodynamic parameters (ΔG remaining essentially unchanged at all temperatures while ΔH and ΔS showed wide fluctuations) and the presence of an isokinetic temperature at ca. 332-338 K indicate that the reaction mechanism involve a donor-acceptor complex. Tabular data summarizing the rate constants and thermodynamic data for the different reactions are included. Figures 2; references 10 (Russian). [395-12172]

UDC 547.241+547.316.3+547.451

REACTION OF ETHOXYMETHYLACETATE AND α -CHLOROMETHYL ETHERS WITH DIALKYLPHOSPHITES AND AMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 27 Aug 82) pp 1541-1544

GRAPOV, A. F. and REMIZOV, A. S., All-Union Scientific Research Institute of
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[Abstract] Ethoxymethylacetate and chloromethyl ether (I) were employed as pseudocarbonyl reagents in reactions dealing with the synthesis of α -aminoalkylphosphonates, by reaction with dialkylphosphites and amines. O,O-diethyl-anilinomethylphosphonate (II) was synthesized by the reaction of I with diethylphosphite (III) and aniline in the presence of triethylamine. The mechanism involved initial formation of N-alkoxymethylaniline which then reacted with III to give II. Reaction of 2-aminopyridine with halomethyl ethers resulted in the formation of alkoxymethylpyridoneimine (IV), and reaction of IV with III resulted in the synthesis of 1-methoxymethyl- and 1-isobutoxymethyl-4-diethoxyphosphoryl-3,4-dihydro-2-pyridones. References 5 (Russian). [395-12172].

CALORIMETRIC STUDY OF HYDROXYETHYLIDENEDIPHOSPHONIC ACID DISSOCIATION UNDER ALKALINE pH

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 14 Jul 82) pp 1544-1549

VASIL'YEV, V. P., KOZLOVSKIY, Ye. V., MAR'INA, T. B. and ORLOVA, T. D.,
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[Abstract] Calorimetric studies were conducted on the dissociation of hydroxyethylidenediphosphonic acid in KOH at pH values ranging from 8.5 to 13.5. Determinations of the stepwise heats of neutralization and dissociation demonstrated that at pH 8.5 the H_2L^{3-} fraction amounted to 94%, the H_3L^{2-} and HL^{4-} fractions for 3% of the salts. The calculated pK and ΔH showed that at the very least the fifth degree of dissociation, i.e., dissociation of the aliphatic hydroxy group proton, did not occur. Thermodynamic data for dissociation at 15, 25, and 35°C are presented in tabular form. References 17: 9 Russian, 8 Western.
[395-12172]

REACTION OF 3,5,8-TRIS(CHLOROMETHYL)-1,4-DIPHOSPHA-2,6,7-TRIOXABICYCLO(2,2,2)OCTANE FRAGMENT-CONTAINING PHOSPHORANES WITH ANILINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 12 Oct 82) pp 1549-1553

MARKOVSKIY, L. N., SOLOV'YEV, A. V., POVOLOTSKIY, M. I. and
SHERMOLOVICH, Yu. G., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Studies were conducted to determine the role of the bicyclooctane structure in the stabilization of phosphoranes. In a series of reactions of trioxydihalophosphoranes and pentaoxyphosphoranes, containing the 3,5,8-tris-(chloromethyl)-1,4-diphospha-2,6,7-trioxabicyclo(2,2,2)octane fragment, with aniline, diazadiphosphetidines were synthesized, the structures of which were confirmed by NMR spectroscopy. The formation of the latter compounds and their stability to hydrolysis were attributed to the stabilizing effects of the bicyclooctane fragment in pentacovalent phosphorus compounds. References 13: 9 Russian, 4 Western.
[395-12172]

SYNTHESIS OF POLYFLUOROALKYL ESTERS OF TRICHLOROMETHYLPHOSPHONIC AND PHOSPHINIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 6 Dec 82) pp 1557-1560

KRUTIKOV, V. I., SEMENOVA, Ye. S., MASLENNIKOV, I. G. and LAVRENT'YEV, A. N.,
Leningrad Technologic Institute imeni Lensovet

[Abstract] Details are presented of experimental studies on the formation of polyfluoroalkyl esters of trichloromethylphosphonic and alkyl- and phenyl-trichloromethylphosphinic acid. The desired target products were synthesized by the reaction of methyl-, ethyl- and phenylphosphinites with carbon tetrachloride in acetonitrile at high temperatures (150-160°C) in a 50% yield. Lowering the reaction temperature to the boiling point of acetonitrile increased the yield to 65-70%. Confirmatory NMR data on the polyfluoroalkyl esters are presented in tabular form. Figures 1; references 4: 3 Russian, 1 Western.
[395-12172]

SYNTHESIS AND STRUCTURE OF 2,2-DIALKYL-1,3-DITHIA-6-PHOSPHA-2-SILACYCLOOCTANES AND P-DIETHYLTRIOORGANYLSILYL(2-MERCAPTOETHYL)PHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 15 Nov 82) pp 1572-1574

UHLIG, V., BARYSHOK, V. P. and VORONKOV, M. G., Irkutsk Institute of Organic Chemistry, Siberian Division, USSR Academy of Sciences; Chemistry Section, Martin Luther University, Halle-Wittenberg, GDR

[Abstract] In order to determine the extent of P → Si coordination in a wide variety of organosilicon compounds, novel compounds in this class were synthesized for NMR studies. 2,2-Dialkyl-1,3-dithia-6-phospha-2-silacyclo-octanes were obtained by the slow addition of P-organylbis(2-mercaptoethyl)-phosphine and dimethylbis(diethylamino)silane in equimolar concentrations to boiling toluene. In a similar manner P-Diethyltriorganylsilyl(2-mercaptoethyl)-phosphines were synthesized by the reaction of P-diethyl(2-mercaptoethyl)-phosphine with triorganylsilanes with triethylamine as HCl acceptor. NMR ¹H, ²⁹Si and ³¹P data indicated that these compounds lack intramolecular P → Si coordination. References 4 (Western).
[395-12172]

PHOSPHADIENES WITH BICOVALENT PHOSPHORUS ATOM

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 9 Nov 82) pp 1672-1673

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Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Phosphadienes with bicovalent phosphorus atom were synthesized by the reaction of P-silylbis(dialkylamino)methylenephosphines with trimethylsilylketene in ether at 0°C with equimolar concentrations of the reagents.

The resultant 2λ³-phospha-1,3-butadienes were represented by yellow-orange liquids that could be vacuum distilled without decomposition. In an analogous manner the reaction of P-silylbis(dialkylamino)methylenephosphine with arylisocyanates resulted in the formation of 1,3λ³-azaphospha-1,3-butadienes. The structure of both classes of compounds were confirmed by chemical analysis and NMR spectra, and PMR data indicate E, Z isomerization. These reactions are the first reported cases of addition of electrophilic reagents into the P-Si bond of methylenephosphine with retention of the coordination number of the phosphorus atom. References 2: 1 Russian, 1 Western.
[395-12172]

REACTION OF METHYLENEDIPHOSPHORUS(III)-CONTAINING ACID CHLORIDES WITH ALDEHYDES AND KETONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 8 Dec 82) pp 1673-1675

NOVIKOVA, Z. S., ODINETS, I. L. and LUTSENKO, I. F., Moscow State University
imeni M. V. Lomonosov

[Abstract] Studies were conducted on the products obtained by the reaction of tetrachloromethylenediphosphine (I) and its derivatives with aldehydes in 1:2 molar ratio in the absence of a solvent. The reactions proceeded exothermally with the formation of bis[α-chloroalkyl(aryl)]methylenediphosphinic acid chlorides (II). Hydrolysis of II with 2 N HCl resulted in the formation of bis[α-hydroxyalkyl(aryl)]methylenediphosphinic acids in 60-80% yield. Under analogous conditions ketones reacted with I very slowly giving a mixture of products with one or two substituents on the phosphorus atom. In the presence of proton-containing reagents, e.g., water or carboxylic acids, the latter reactions proceeded exothermally with the formation of bis[α-hydroxyalkyl(aryl)]methylenediphosphinic acid chlorides which, on hydrolysis with HCl, gave bis[α-hydroxyalkyl(aryl)]methylenediphosphinic acids. Product structures were confirmed by chemical analysis and NMR and PMR spectroscopies.
References 4: 3 Russian, 1 Western.
[395-12172]

REACTION OF PHOSPHORUS PENTACHLORIDE ADDUCTS WITH CARBOXYLIC ACID SALTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 8 Dec 82) pp 1677-1678

MITRASOV, Yu. N. and KORMACHEV, V. V., Chuvash State University imeni
I. N. Ul'yanov

[Abstract] Adducts of phosphorus pentachloride and unsaturated compounds (1-alkene, styrene, phenylacetylene, vinyl alkyl ethers, dialkyl ethers, tetrahydrofuran, tert-butanol) reacted with acetic acid salts to yield alkenylphosphonic acid dichlorides. In this manner dichlorides of the following acids were synthesized: 2-ethoxyvinylphosphonic acid, 2-chloro-2-phenylvinylphosphonic acid, and 2,3-dihydrofurfuryl-4-phosphonic acid. Salts of formic and oxalic acids did not react with the adducts even at 40°C. References 4 (Russian).

[395-12172]

REACTION OF TRIS(1,1,3-TRIHYDROTETRAFLUOROPROPYL)PHOSPHITE WITH ACETYL BROMIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 18 Jan 83) p 1678

ALEYNIKOV, S. F., KRUTIKOV, V. I., GOLOVANOV, A. V., MASLENNIKOV, I. G. and LAVRENT'YEV, A. N., Leningrad Technologic Institute imeni Lensovet

[Abstract] The reaction of tris(1,1,3-trihydrotetrafluoropropyl)phosphite with a three-fold molar excess of acetyl bromide for 8 h in sealed ampules at 140°C resulted in the formation of PBr_3 and 1,1,3-trihydrotetrafluoropropyl acetate. The products appeared in two well demarcated layers, with PBr_3 in the lower layer. References 5: 3 Russian, 2 Western.

[395-12172]

REACTION OF PHOSPHORUS PENTASULFIDE WITH α, α, ω -TRIHYDROPERFLUOROALKANOLS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 53, No 7, Jul 83
(manuscript received 15 Dec 82) p 1679

KROLEVETS, A. A.

[Abstract] Studies were conducted which showed that the reaction of P_2S_5 with α, α, ω -trihydroperfluoroalkanols at 150-170°C leads to the formation of bis- α, α, ω -trihydroperfluoroalkyl dithiophosphates. The latter are light-yellow transparent liquids that decompose at >200°C. The structures of these compounds were confirmed by IR and NMR spectroscopies. References 1 (Russian). [395-12172]

UDC 541.128.34.665.644.2.661.183.6

COMPARATIVE ACTIVITIES AND SELECTIVITIES OF SVK ZEOLITE AND FOZHAZITE
[SIC] IN n-OCTANE CRACKING

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57, No 8, Aug 83
(manuscript received 15 Feb 82) pp 1994-1997

YUSHCHENKO, V. V., TOPCHIEVA, K. V., MEGED', N. F. and LIMOVA, T. V.,
Chemical Faculty, Moscow State University imeni M. V. Lomonosov

[Abstract] Comparative studies were conducted on the activities and selectivities of the SVK zeolite Ultrasil and SaNu fozhazite [sic] in cracking n-octane. The calculated rate constants with Ultrasil were significantly higher than with fozhazite. In the case of both catalysts the paraffin yield falls and that of olefins increases as the degree of conversion diminishes on both catalysts. n-Butane formation on Ultrasil takes place in the primary cracking of the $n\text{-C}_8\text{H}_{19}^+$ carbocation, and in the case of fozhazite as a secondary process due to hydrogen transfer from the n-octane molecules and olefins during formation of condensation products. The $\text{iso-C}_4/\text{n-C}_4$ ratio on Ultrasil is much lower than on fozhazite because, in the former case, rearrangement of the long-chain carbocations is retarded by the narrow channel system of Ultrasil. References 10: 4 Russian, 6 Western.
[401-12172]

UDC 678.01:537.311.33

TRANSFER PROCESSES IN ELECTRIC CONDUCTOR DISPERSION-FILLED POLYMER COMPOSITES

Moscow USPEKHI KHIMII in Russian Vol 52, No 8, Aug 83 pp 1336-1349

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USSR Academy of Sciences, Moscow

[Abstract] The need for materials combining properties of metals, semiconductors and polymers has been satisfied by synthetic polymers with new chemical structures or by introducing electric conductor fillers in dielectric polymers. The present survey concentrates on transfer processes in such composites, with discussion centering on such electric conductor fillers as Cu, Al, Ni, Zn, Au and Ag fillers, graphite and technical charcoal or soot. The mechanism of electric conductivity of polymer composites, which are unordered systems structurally, and the relationship between component properties and properties of the whole are discussed. The most realistic mechanism is regarded to be fluctuational tunneling. Bonding of electric conductor filler particles in composites is evaluated using an approach developed for graphite. The most general approach for describing conductivity in amorphous systems is the percolation theory, which is illustrated by the transition from dielectric to semiconductor in granular metals. The subject of structured composites obtained by pressing powdered polyethylene or polypropylene and metals completes the discussion of mechanisms. Methods of preparing composites and their electric conductivity, and application of conductive composites are also noted. One of the basic problems in studying such composites is considered to be the fact that they cannot be studied within normal model frameworks. Another is the need for establishing inter-phase contacts for making measurements. Properties of fillers and polymers, distribution of fillers and the type of contact between components also require further clarification. Figures 10, references 62: 32 Russian, (2 translations from English), 30 Western.
[403-12131]

METAL CLUSTERS IN POLYMER MATRICES

Moscow USPEKHI KHIMII in Russian Vol 52, No 8, Aug 83 pp 1350-1364

GUBIN, S. P. and KOSOBUDSKIY, I. D., Institute of Inorganic Chemistry, Siberian Division, USSR Academy of Sciences, Novosibirsk

[Abstract] Polymers with desirable electrophysical properties are difficult to obtain in large quantities. As a result, research has turned in the direction of "doping" polyethylene and teflon with donor and acceptor coatings, such as clusters of transitional metals, in order to obtain metal-polymer compositions. This research has resulted in a new type of materials labelled "klaspol" [from cluster-polymer]. These compositions are obtained by such methods as electro-chemical reduction of metals from solutions in the presence of surface-active substances (SAS), mechanical chemical synthesis based on the high surface activity found during metal dispersion, displacement, and thermal synthesis. Other approaches include plasma chemical and cryochemical methods. The effect of dispersed fillers on polymer properties and structure relate to the amorphous structure and the importance of "vacancy" dimensions in the initial polymers. Methods of synthesis for "klaspol" materials involve control with differential thermal analysis, X-ray phase analysis, infrared and NMR spectroscopy and other procedures. Structure and physico-mechanical properties are discussed in terms of X-ray and Messbauer investigations of metal clusters in polymer matrices, the effect of metal clusters on the polymer structure as determined by NMR spectra, physicochemical, electrophysical and magnetic properties of "klaspol" materials. Figures 10, references 62: 42 Russian, 20 Western.
[403-12131]

TECHNOLOGY, STRUCTURE AND PROPERTIES OF ORGANIC SILICON DIELECTRICS-POLYORGANOSILSESQUIOXANES

Moscow USPEKHI KHIMII in Russian Vol 52, No 8, Aug 83 pp 1365-1409

TON'SHIN, A. M., KAMARITSKIY, B. A. and SPEKTOR, V. N., Moscow State Pedagogical Institute imeni V. I. Lenin; Moscow Institute of Precision Chemical Technology imeni M. V. Lomonosov; Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] The authors survey applications of dielectric materials in numerous branches of the economy in sections on electronic instruments, where for example the SiO_2 -Si system has meta-stable defect compensation determined by formation conditions, synthesis and technology for producing oligo-organosilsesquioxanes with small aliphatic and aromatic radicals, optimization of continuous hydrolytic condensation of organochlorosilanes, a shell model for

that process, optimization of continuous production of oligo-organosilsesquioxanes through molecular weight distribution and high purity versions of such oligomers, and modifications of these compounds. Polycondensation processes are outlined in numerous steps. Questions of reactions of these compounds that have solid heterophases include mixed compositions based on organic silicon binders, cocondensation of mono- oligo- and polyorganosiloxanes with surface functional groups, and reaction mechanism with a monocrystalline silicon surface and possible polymer filling. Further sections are devoted to the structure of cyclo-, oligo- and polyorganosilsesquioxanes, including molecular structure and phase composition, laminate and coating adhesion characteristics, and electrophysical properties in terms of tunnel electrical conductivity of amorphous systems, dielectric spectroscopy, polarity and the electric effect. In conclusion, the authors point to the need for predictable physicochemical characteristics in producing soluble and fusible oligomers. Figures 10; references 281: 233 Russian, 48 Western. [403-12131]

UDC 541.64+678.763.2

STUDY OF POLYMERIZATION OF CHLOROPRENE IN ORGANIC SOLVENTS

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 36, No 7, Jul 83
(manuscript received 21 Apr 82) pp 467-471

VOSKANYAN, E. S., GASPARYAN, L. E. and GASPARYAN, S. M., "Nairit" Scientific-Production Association, Yerevan

[Abstract] Results are presented from polymerization of chloroprene in solvents which dissolve both the monomer and polymer; the influence of certain factors on the process have been studied. Freshly distilled chloroprene with purity chromatographically verified was used. Azoisobutyric acid dinitrile was purified by recrystallization from absolute methanol, the solvents by various known methods yielding a purity of at least 99.9%. Kinetic measurements of the polymerization of chloroprene were performed in air. The highest polymerization rate was observed in carbon tetrachloride. The chloroprene polymers produced in organic solvents were primarily liquid, quite stable, not changing their properties or solubility for long periods of time. In contrast to emulsion polychloroprene, the polymers obtained in the solvents had a low degree of crystallization. These polymers can be used to produce halogenated polychloroprenes, various adhesive and varnish compositions, adhesive tapes, etc. With CCl_4 as solvent, a method was developed for producing chlorinated polychloroprene equivalent in its properties to the product obtained from high molecular series produced nairite-chloronairite. Figures 5; references 12: 10 Russian, 2 Western. [405-6508]

INFLUENCE OF TYPE AND QUANTITY OF CERTAIN RADICAL INITIATORS AND CHAIN REGULATORS ON POLYMERIZATION OF CHLOROPRENE IN SOLVENTS

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 36, No 7, Jul 83
(manuscript received 21 Apr 82) pp 471-476

VOSKANYAN, E. S. and GASPARYAN, L. E., "Nairit" Scientific-Production Association, Yerevan

[Abstract] Continuing their work on polymerization of chloroprene and other halogen dienes in organic solvents, the authors studied the influence of the type and quantity of radical initiators and chain regulators on polymerization of chloroprene. The chloroprene used was freshly distilled and the initiators, regulators and solvents obtained in purified form. Kinetic measurements were performed by known methods with repeatedly polymerized chloroprene. Azoisobutyric acid dinitrile had the greatest influence on polymerization of chloroprene and was therefore studied in greatest detail. In contrast to emulsion polymerization, when the process is performed in organic solvents, an increase in the quantity of dodecylmercaptan regulator from 0.5 to 2 mass % caused comparatively little change in molecular mass. Also, the difference between the regulating capacity of tert- and n-dodecylmercaptans was greater. Varying the type and quantity of initiator and regulator in addition to the quantity and type of solvent can yield low-molecular-weight polymers and oligomers of chloroprene with a broad range of molecular mass. Figures 3; references 9 (Russian).
[405-6508]

FRICTIONAL PROPERTIES OF FIBERGLASS FILLED THERMOPLASTICS MODIFIED WITH POLYETHYLENE ADDITIVES

Kiev DOKLADY AKADEMII NAUK UKRAINSKOY SSR, SERIYA B: GEOLOGICHESKIYE, KHIMICHESKIYE I BIOLOGICHESKIYE NAUKI in Russian No 7, Jul 83
(manuscript received 29 Mar 83) pp 32-34

GLADCHENKO, A. N., PETRENKO, S. D. and PRIVALKO, V. P., Institute of High Molecular Compounds Chemistry, UkSSR Academy of Sciences

[Abstract] In an attempt to determine optimal composition of fiberglass filled thermoplastics modified with polyethylene (PE), the following characteristics were studied as functions of temperature: rigidity modulus at compression E , friction coefficient f , wear I and wearability i . Industrial samples of polyamide, polyhydroxymethylene and polycarbonate were studied. It was shown that addition of 4% of PE resulted in a decrease of I and i in all samples. Evidently, the lubricating layer of PE deactivated macroradicals forming in the frictional contact zone due to mechanical destruction of polymer matrix. Figures 2; references 6 (Russian).
[384-7813]

PRODUCING HOLLOW POROUS POLYPROPYLENE FIBERS WITH HIGH GAS PERMEABILITY

Moscow KHIMICHESKIYE VOLOKNA in Russian No 4, Jul-Aug 83
(manuscript received 27 Sep 82) pp 12-14

MATROSOVICH, M. N., ANDREYEV, V. G., KOSTROV, Yu. A. and BUDNITSKIY, G. A.

[Abstract] Porous polymer films and hollow fibers with pores of 50-1000 Å dimensions, used for isolating various substances, were produced by the creation and study of so-called rigid elastic polymers that have microscopic porosity when stretched in a single direction. Production stages included use of flexible link crystallized polymers to form films or hollow fibers under great stretching and sharp cooling, annealing at 10-15° below the polymer's melting point, "cold stretching" by 50-200% in a direction perpendicular to the crystal laminations, and finally, thermal fixing of the film or fiber. Transport properties of these polymers for various gases at 101 kPa pressure and 25°C temperature were then studied. Temperature during stretching and cooling rate were found to be important parameters in the production of these polymer materials. The optimum fixation temperature was found to be 135-145°C. The polymers had high gas permeability and could find applications as ultrafilters, microfilters, after proper preparation as reverse osmotic membranes, and in mass transfer in a gas-liquid system. Further development and selectivity is required. Figures 3; references 9: 3 Russian, 6 Western.
[406-12131]

UDC 677.862:678.632

MODIFYING POLYAMIDE FIBERS BY FORMING MUTUALLY PERMEABLE POLYMER SYSTEM IN SURFACE LAYER

Moscow KHIMICHESKIYE VOLOKNA in Russian No 4, Jul-Aug 83
(manuscript received 18 Oct 82) pp 14-16

LIPATOV, Yu. S., SERGEYEVA, L. M., NOVIKOVA, O. A. and GLUKHOVSKAYA, M. I.

[Abstract] The authors developed a method for modifying the mutually permeable polymer system in the upper layer of a phenolformaldehyde resin polymer. The resulting composite had polyamide and hardened phenolformaldehyde resin layers, which were then tested for density by a hydrostatic suspension method, as well as for melting point and deformation durability characteristics at various temperatures. The swelling of the capron fibers in the phenolformaldehyde oligomer increased the melting point by forming a three-dimensional structure. The density and heat resistance of the resulting polymer also improved at room temperature and 60, 100 and 140°C. The best absolute values were noted for fibers with 22% hardened polymer modifier in the surface layer. Figures 3; references 5: 4 Russian, 1 Czech.
[406-12131]

STRUCTURAL FEATURES OF TRANSPARENT POLYAMIDE MONOFILAMENTS

Moscow KHIMICHESKIYE VOLOKNA in Russian No 4, Jul-Aug 83
(manuscript received 2 Dec 82) pp 17-20

SEMENOVA, T. P., SKOPINTSEVA, V. N., ISAYEVA, V. I., FIL'BERT, D. V. and
KABANOV, V. N.

[Abstract] Previously, the authors had produced transparent monofilaments from polycapromide by introducing modifiers into the fiber-forming polymer. In the present study they considered the effect of modifier nature and quantity on monofilament structure and transparency using N,N'-dibenzoyl-4,4'-diaminodiphenyloxide, 2-hydroxy-4-ethoxyphenylheptadecylketone or N,N'-distearoyldiaminodiphenylanthrone. Compounds that facilitated the formation of a finely structured surface were regarded to be retardants of crystallization. Of the modifiers, the first brought some improvement of spherulite structure, while the second speeded crystallization. The effects of arylaliphatic ketones and diamides and aliphatic diamides as crystallization retardants, and thus promoters of transparency, were maintained after stretching. A 0.5%-by-weight addition of a modifier was judged to be the optimum for forming a fine granular surface. Figures 3; references 7: 6 Russian, 1 Western. [406-12131]

UDC [677.494.675:536.495]019.394

STUDY OF THERMAL DURABILITY OF POLY-P-PHENYLENETEREPHTHALAMIDE FIBERS

Moscow KHIMICHESKIYE VOLOKNA in Russian No 4, Jul-Aug 83
(manuscript received 5 Jan 83) p 21

DOVBIY, Ye. V., KHUDOSHEV, I. F., KALASHNIK, A. T., PAPKOV, S. P.,
VOLOKHINA, A. V. and KUDRYAVTSEV, G. I.

[Abstract] The authors studied rigid-link polymer fibers, which have many valuable characteristics, including high durability, to determine the effects of high temperatures on chemical bonds. Electron spin resonance and thermal analysis were made of fibers based on poly-p-phenyleneterephthalamide before and after heating at 250°C for 100 hours. The fibers received no heat treatment before the tests. Results showed an increase in paramagnetic centers, apparently due both to tension developed in the polymer chains and to the breakdown of chemical bonds in the chains. The net result was a loss of durability. Figure 1, references 4 (Russian). [406-12131]

FILTERABILITY OF COPPER-AMMONIA CELLULOSE-SOLUTIONS THROUGH BARRIERS WITH VARIOUS PORE SIZES

Moscow KHIMICHESKIYE VOLOKNA in Russian No 4, Jul-Aug 83
(manuscript received 3 Dec 82) p 30

TAMARKOVA, N. A., FINGER, G. G., SURNINA, Z. A., BAKSHEYEV, I. P. and
PAKSHVER, A. B.

[Abstract] Recent high-production methods for copper-ammonia fibers require increased purity of the spinning solution. The authors studied the effect of spinning solution composition on retarding of filtration through a filter with 23, 40 and 71 mkm pores, with a constant pressure decrease at the filter barrier. The solutions had a constant NH_3 /cellulose ratio of .65, and Cu/cellulose content was varied. Increasing the ratio of copper to cellulose was found to affect filterability, particularly with small pores. Heating the solution above 40°C caused considerable retardation of permeability, while at 70°C, or above, CuO formed that blocked the pores entirely. Viscosity was also found to be an important factor when small pore sizes were used in the filters. Figures 2.
[406-12131]

USE OF POROUS POLYMER SORBENTS FOR CONCENTRATING MICRO-IMPURITIES OF ORGANIC COMPOUNDS FROM GAS AND LIQUID MEDIA

Moscow USPEKHI KHIMII in Russian Vol 52, No 7, Jul 83 pp 1225-1246

GLAZUNOVA, L. D., PANINA, L. I. and SAKODYNSKIY, K. I., Scientific Research
Physico-Chemical Institute imeni L. Ya. Karpov, Moscow

[Abstract] Control of air and water pollution from industrial and home sources requires identification and removal of trace impurities. Their identification in air and water requires selection and storage of samples, concentration of components and chromatographic analysis. These procedures are discussed in sections on basic methods for concentrating micro-impurities of organic compounds using a liquid extraction, freezing, chemical location and adsorption sequence, for air, and adding a thermal step in analyzing water impurities; selection of sorption material for preparing concentrate samples, porous polymer sorbents in the adsorption method of micro-impurity concentration; and solutions to special problems posed by porous polymer sorbents. Basic features of sorbents, preparation of sorbents for concentration processes, sorption capacity, extraction percentage and preservation of concentrated impurities are discussed. Specific sorbent materials discussed include "Tenex", "Porapak", "Chromosorb" and "Sferon". The final sections of this discussion deal with extraction of micro-impurities and use of domestic (Soviet) porous polymers as

sorbents. Many of these sorbents (both imported and domestic) can be recycled and reused. They offer effective and economical means for combating air and water pollution. References 106: 14 Russian, 92 Western. [379-12131]

UDC 678.744:678.01:53

STUDY OF PRODUCTS OF INTERACTION OF A STATISTICAL COPOLYMER OF ACRYLIC ACID--METHYLACRYLATE WITH POLYVINYLPIRROLIDONE AND POLYETHYLENEGLYCOL IN SOLUTIONS

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 83 (manuscript received 1 Sep 81) pp 27-31

FROLOVA, V. A., BIMENDINA, L. A. and BEKTUROV, Ye. A., Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Conductometric and potentiometric titration methods were used to study interpolymer complexes of non-ionogenic polymers (polyvinylpyrrolidone and polyethyleneglycol) with a statistical copolymer of acrylic acid and methylacrylate in water, methanol and dimethylformamide. It was found that complexes of an acrylic acid/methylacrylate copolymer with polyvinylpyrrolidone in water are stronger than those with polyethyleneglycol and more stable than complexes forming in methanol and dimethylformamide. Properties of complexes of statistical copolymers of acrylic acid/methylmethacrylate and acrylic acid/methylacrylate with polyvinylpyrrolidone and polyethyleneglycol were found to be quite similar. There was an upper critical limit of molecular masses of polyethyleneglycol above which complex formation for a system of polyethylene--copolymer of acrylic acid with methylacrylate--water was impeded. Figures 4; references 7 (Russian). [381-2791]

UDC 678.744:678.01:53

HYDRODYNAMIC PROPERTIES OF SOLUTIONS OF A STATISTICAL COPOLYMER OF ACRYLIC ACID AND METHYLMETHACRYLATE WITH A COMPOSITION OF 77:23 MOLE PERCENT

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 83 (manuscript received 21 Sep 81) pp 31-34

YEL'CHIBAYEVA, Z. S., BAKAYOVA, Z. Kh., BEKTUROV, Ye. A. and DZHUMADILOV, T.K., Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Viscosity characteristics and sedimentation constants of fractions of a copolymer of acrylic acid and methylmethacrylate containing 77 mole percent acrylic acid were measured in dimethylsulfoxide, 0.005 n-KI in dimethylformamide, 0.005 n-KI in methanol and 0.075 n-KCl. The viscosity in 0.075 n-KCl was 7 or 8 times less than that in dimethylsulfoxide, dimethylformamide

and methanol. High values of characteristic viscosity in methanol, dimethylsulfoxide and dimethylformamide are due to the strong interaction of the copolymer with these solvents via hydrogen bonds. The polymer dissolved in water because of the low level of methylmethacrylate. Addition of an organic solvent to the water destroyed the secondary structure which macromolecules of the copolymer evidently possess in water because of the presence of methylmethacrylate sections. Figures 2; references 11: 9 Russian, 2 Western. [381-2791]

UDC 541.127+547.313.3

POLYMERIZATION OF PROPYLENE ON MODIFIED COMPLEX CATALYSTS PRODUCED ON THE
BASE OF COMMERCIAL HIGHLY-DISPERSED $\delta\text{-TiCl}_3 \cdot 0.3 \text{ AlCl}_3$

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA
in Russian No 4, Jul-Aug 83 (manuscript received 12 Sep 81) pp 57-63

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[Abstract] A study of polymerization of propylene on modified samples of $\delta\text{-TiCl}_3 \cdot 0.3 \text{ AlCl}_3$ in combination with aluminum alkyls showed that washing with hot n-heptane (100°C and 150°C for one hour) with use of AlEt_2Cl as a cocatalyst increases the activity by 10-15 percent and 30 percent respectively. The kinetics of polymerization with AlEt_3 , $\text{Al}i\text{Bu}_3$ and AlBu_2H appeared to be unsteady and differed greatly in form from that seen with the use of AlEt_2Cl . A catalyst with activity and stereospecificity of the same order of magnitude as that found after processing at 100°C was produced by use of $\delta\text{-TiCl}_3 \cdot 0.3 \text{ AlCl}_3$ processed by heptane solutions $(\text{C}_5\text{H}_{11})_2\text{O}$ at 20°C for 1 hour. Washing $\delta\text{-TiCl}_3 \cdot 0.3 \text{ AlCl}_3$ with solutions of $(\text{C}_2\text{H}_5)_2\text{O}$ and $(\text{C}_5\text{H}_{11})_2\text{O}$ in heptane at 100°C doubled the catalyst (with AlEt_2Cl) activity. The change of rate was exponential even with AlEt_2Cl . Isotacticity of the polypropylene reached 97-98 percent. Figures 3; references 20: 15 Russian, 5 Western. [381-2791]

UDC 541.64:539.2

SOME KINETIC REGULARITIES OF FORMATION OF IMPACT RESISTANT EPOXY-RUBBER COMPOSITIONS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 26, No 7, Jul 83 (manuscript received 4 Oct 82) pp 888-889

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[Abstract] A study was made of the specifics of modification of carboxyl-containing raw rubbers by epoxy polymers cured by phenol Mannich bases. Analysis of the experimental data on modification of epoxy oligomer ED-20 cured with dimethylaminomethylphenols with varying contents of tertiary nitrogen by the introduction of polybutadiene raw rubbers with terminal carboxyl groups showed the prevalent influence of technological factors on the deformation and strength properties of the epoxy materials produced. With the traditional modification technology, introduction of raw rubber to the epoxy composition before the curing agent, the effect of elastification is almost nil. When the raw rubber is mixed first with the curing agent and then this mixture is added to the epoxy oligomer, a significant increase in impact toughness is observed. The maximum impact toughness is achieved with a minimum value of polymerization process activation energy and maximum heat liberation. The activation energy of the polymerization process can thus be used as a kinetic parameter for optimization of the modification technology. Figure 1; references 6: 3 Russian, 3 Western.

[409-6508]

PRODUCING CHEAP ADSORBENT FOR PURIFYING SEWAGE

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul-Aug 83
(manuscript received 1 Dec 81) pp 126-129

KOCHETKOVA, R. P., EPPEL', S. A. ZHDANOVA, K. P., VDOVENKO, T. A. and
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[Abstract] Sewage treatment with activated charcoal is very effective, but its implementation is limited by low production of such adsorbents, ineffective recycling methods, high costs and low mechanical durability. The present study investigates the possibility of producing low-cost carbon sorbents from semicoke of Cheremkhovskiy coals. The initial semicoke had 36% ash, poor porous structure and insufficient adsorptive characteristics. Activation was conducted in a quartz column of 850-1000 mm length and 30-32 mm diameter, equipped with a spiral electric heater and a steam-gas feed system for the activating agent, carbonic acid gas and water vapor. Temperature and combustion loss factors determined the rate of activation and the development of the porous structure, respectively. Results showed that the temperatures of 700, 800 and 900°C produced activated charcoal with similar capacity for phenols and summary phenols of tar waters, with processing time decreasing with increasing temperature. The optimum parameters were judged to be 800-850°C for 3.5-4 hours with 1.25 g of both water vapor and carbonic acid gas per gram of initial semicoke. Greatly reduced cost and improved durability were achieved. Figures 3; references 4: 3 Russian, 1 Western.
[376-12131]

UDC 630*863.5:663.14.039.3.002.235

MEASURES TO ELIMINATE SHORTAGES AND INCREASE FEED PROTEIN PRODUCTION

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST' in Russian No 5,
Sep-Oct 83 pp 1-2

Editorial staff

[Abstract] In implementing the USSR Food Program, institutions involved in microbiological production, including hydrolysis plants, are being expanded; capabilities of plants of the All-Union Production Association "Soyuzgidroliz-prom" are being improved. However, problems such as improper utilization of existing facilities and resources and management shortcomings of various types stand in the way. There is high labor turnover, resulting in technical production delays and waste. Construction projects and research suffer as well from such difficulties. For example, the two-phase hydrolysis operation at the Manturovskiy Biochemical Plant is unstable. Improvements are crucial in production of industrial yeast strains and other elements of the raw material base of the industry. Feed sugars for livestock, including sugar beet, molasses and other industrial sugar crops require further development. Research needs range from preliminary studies to veterinary toxicological testing.
[377-12131]

UDC 630*863:547.724.2.061.3

REPORT ON ALL-UNION SCIENTIFIC COUNCIL ON THE PROBLEM TOPIC USE OF PENTOSAN-CONTAINING RAW MATERIALS

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST' in Russian No 5,
Sep-Oct 83 pp 3-4

Editorial staff

[Abstract] New uses for furfural, beyond customary petroleum processing, include furfuryl and tetrahydrofurfuryl alcohols, tetrahydrofuran, polyfurfite and various resins used for heat-resistant electrical insulation, lacquers, glues for metals and other materials and binders in mastics and cements. Both foreign and domestic Soviet applications have been found in herbicides, insecticides of low toxicity, chemotherapeutic and pharmacological preparations. The All-Union Scientific Council on the Problem Topic Use of Pentosan-Containing Raw Materials, held in Yurmala, Latvia in April 1983, heard reports

on continuous production of furfural with concurrent dehydration of pentose, on procedures for recovering at least 75% of the furfural contained in raw materials and research in finding new sources for furfural, such as utilization of prehydrolysates of deciduous wood processing, improved documentation and data processing, use of corn cobs as raw material in appropriate southern hydrolysis plants, improved transportation and a number of specific plant improvement and process modernization projects. Research, particularly on use of plant residue from cotton, grains and vines, and replacement of feed materials with non-feeds as raw materials, will continue and will be the subject of a planned All-Union conference in 1984 or 1985.
[377-12131]

UDC 630*863:547.724.2.004.14

SYNTHESIS AND USE OF FURFURAL PROCESSING PRODUCTS

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST' in Russian No 5, Sep-Oct 83 pp 4-6

SHIMANSKAYA, M. V., doctor of chemical sciences, deputy chairman, All-Union Scientific Research Council on the Problem Topic Use of Pentosan-Containing Raw Materials, LaSSR Academy of Sciences

[Abstract] Broad research on synthesis and uses of furan includes study of the key compound of the numerous plant annuals that can serve as raw materials, to determine specific reactions and applications. This survey covers developments in various fields over the past 10-20 years. Medical preparations based on the diacetate of 5-nitrofurfural have urological, gynecological and trauma applications, while related products are effective for staphylococcal and bacterial infections, dysentery, Salmonella and other septic ailments. Derivatives of 5-nitro-2-furylalkylketones and related compounds are being studied for specific antibacterial applications. The anticarcinogen "Ftorafur" is produced from 2-chlorofuranidine (derived from furan intermediates). Furan derivatives containing silicon have been found to have psychotropic effects. Agricultural products based on furfural are being developed for herbicidal, growth regulation and veterinary medical uses. Monomers synthesized from furans make furfurylic and tetrahydrofurfurylic alcohols, sylvan and tetrahydro-sylvan. The alcohols are used to make resins with high adhesion and acidity, impermeability to gas and water and other useful characteristics. References 23: 21 Russian, 1 Czech, 1 Western.
[377-12131]

INCREASED PRODUCTION OF FURFUROL REQUESTED

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST' in Russian No 5,
Sep-Oct 83 pp 12-13

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[Abstract] The development of furfural production at the Kropotinskiy Chemical Plant is traced since 1966. Currently, corn cobs, sunflower stalks and rice husks are used as raw materials. Features of the furfural-hexose hydrolysis process include grinding corn cobs to 20 X 20 X 20 mm pieces, treatment in 8-10% sulfuric acid solution, and hydrolysis at 260-270°C and 1.5 MPa. While furfural production from corn cobs is in full operation at the plant, the problems of high labor input and seasonal material supply remain. The bottleneck of removing ready furfural from the hydrolysis equipment before it can decompose is being attacked by installing 150 mm diameter steam input and output lines instead of the current 110 mm pipes. Labor and technical problems are also cited, but a key need is year-round raw material supply.
[377-12131]

CSO: 1841

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